THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 1 FEBRUARY, 1933 NUMBER 2

Mass-Spectrograph Study of the Ionization and Dissociation by Electron Impact of *n*-Octane

ERNEST G. LINDER,* *RCA Victor Company, Inc., Camden, N. J.*

(Received December 2, 1932)

A mass-spectrograph study of *n*-octane (C_8H_{18}) indicates that when bombarded by 120 e-volt electrons, it dissociates into a large number of small fragments, of which those containing two or three carbon atoms (and some hydrogen) are most numerous. Ions containing odd numbers of H atoms are produced in larger quantities than those containing even numbers. The octane molecule displays a greater tendency to break up than does benzene (reported in a previous paper), which is in accordance with the reactions of these compounds in gaseous electrical discharges.

IN a recent article in *The Physical Review*[1] the writer reported an investigation of the ionization and dissociation of benzene (C_6H_6) by electron impact. The present paper deals with a similar study of *n*-octane (C_8H_{18}). These two compounds are representative of two important groups of hydrocarbons, the aromatics and the normal paraffins. The aromatic group, of which benzene is a member, is characterized by a molecular structure built up principally of units consisting of rings of six carbon atoms (the benzene ring). On the other hand, the normal paraffin molecule consists of a straight chain of carbon atoms. In each case, of course, the appropriate number of hydrogen atoms also are present.

These two classes of compounds have been found by Linder and Davis[2] to behave in quite different fashions in chemical processes taking place in electrical discharges. Aromatics tend to polymerize, that is, the original molecules combine to form larger aggregates. This usually results in the formation of complex resins and waxes. There is not much breaking up of the original compound. However, paraffins behave in the opposite fashion. That is to say, there is considerable breaking up of the molecule and many compounds of molecular weight less than that of the original are formed. A larger part of the reaction products are gaseous, than in the case of an aromatic compound of similar molecular weight.

The mass-spectrograph studies of these two compounds carried out by the writer indicate that these characteristic modes of reaction may be attributed in a large part to the primary effect of electron bombardment rather than to succeeding secondary reactions. This follows since primary ions observed show that the benzene molecule tends to remain whole, whereas the octane molecule tends to break up immediately upon impact and without further collisions of any sort.

The data on *n*-octane are given in Fig. 1 and Table I. In Fig. 1 current through the magnet is plotted against electrometer deflection. The

* Formerly Detroit Edison Research Associate at Cornell University. The work reported in this article is a part of an investigation of the fundamentals of the disintegration of organic dielectrics being carried on at Cornell and supported financially by the Detroit Edison Company.

[1] Ernest G. Linder, Phys. Rev. **41**, 149 (1932).

[2] Linder and Davis, J. Phys. Chem. **35**, 3649 (1931).

eight groups of peaks correspond to ions having carbon atoms in number from one to eight. The large numeral over the group indicates the number of carbon atoms in the ions of that group, while the small numeral over the individual peaks in each group indicates the number of hydrogens corresponding to that peak. For example, the highest peak in the figure has, according to the labels, the formula $C_3H_7^+$.

TABLE I. *Ion group percentages for n-octane* ($V = 120$ *volts*).

Ion group	Pressure (mm Hg$\times 10^3$) 0.7	3.7	4.0	4.5	5.1	7.7
1*C*	1.2	0.5	1.5	2.5	0.9	1.2
2*C*	14.4	10.4	18.4	13.4	15.3	20.4
3*C*	34.8	31.5	29.7	35.1	35.6	28.2
4*C*	18.2	15.7	17.9	12.4	14.0	14.8
5*C*	8.4	11.3	9.6	7.8	9.7	10.5
6*C*	11.5	20.0	14.5	9.6	15.9	15.0
7*C*	3.7	2.0	1.1	1.3	0.0	0.7
8*C*	7.8	8.9	7.3	17.9	8.6	9.2

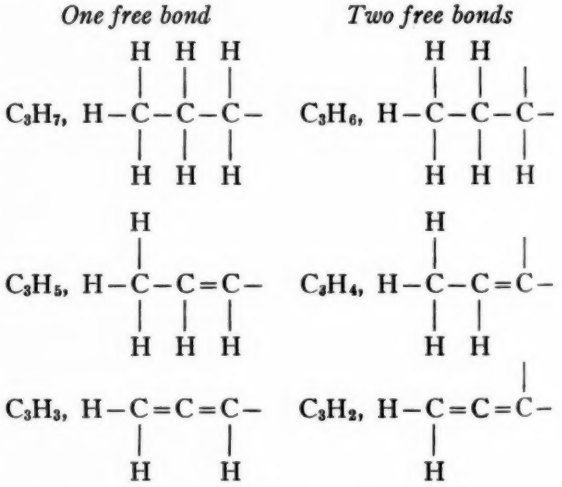
The peaks for H_2O^+ and OH^+ were prominent only in the runs made just after the apparatus was sealed to the pumps and exhausted. Water vapor is known to be very difficult to remove, especially when the apparatus is of a type that cannot be baked out, as in the present case. In making some of the runs the mercury pumps were run continuously for two weeks, and in this case the water peaks disappeared after about two days and could not be detected thereafter. Upon readmitting atmospheric air, again pumping out, and making a run, the water peaks reappeared.

The small benzene peak likely arose from traces of that substance absorbed in the apparatus, especially in the waxes used in making some of the seals, and carried over from previous runs on benzene. This peak also disappeared, becoming undetectable after two days of pumping.

The octane was obtained from the Eastman Kodak Company. It was dried with sodium wire and distilled. Six fractions were taken. A part of the fourth fraction, which boiled in the range 124.4–124.8°C, was used for the mass-spectrograph work.

The most striking feature of the analysis of octane in comparison with that of benzene is the greater dissociation of the former into small fragments. In the case of benzene, the principal ion was found to be a complete benzene molecule, but in the present case the principal ions are fragments having only two or three carbon atoms. This is in entire agreement with the reactions of paraffin and aromatic hydrocarbons in the glow discharge and Siemen's discharge.[2] It indicates that the large gas production of the paraffins is due at least in a large part to primary reactions in which the molecule is broken into fragments, which appear as gases or lighter liquids in the final products.

Another striking feature, exhibited by the 2*C* and 3*C* peaks, is the alternation of large and small peaks. In the 3*C* peak for example, the peaks of hydrogen content 1, 3, 5 and 7 are intense, whereas the 2, 4 and 6 are weak. This phenomenon was found not to vary with pressure and hence appears to be a primary effect. It would seem therefore that the hydrogen atoms tend to come off in pairs. It is worth noticing that the ions formed when the hydrogens thus come off have fewer free valence bonds than when they come off singly. This is made clear by the following diagram.



Obviously the ions having odd numbers of hydrogens, have only one free bond, whereas those having even numbers of hydrogens have two free bonds. The latter are probably the less stable, and according to the data are formed in fewer numbers, as should be expected.

Of course the structures given in the above diagram are not the only ones possible for those particular empirical formulas. Their only virtue

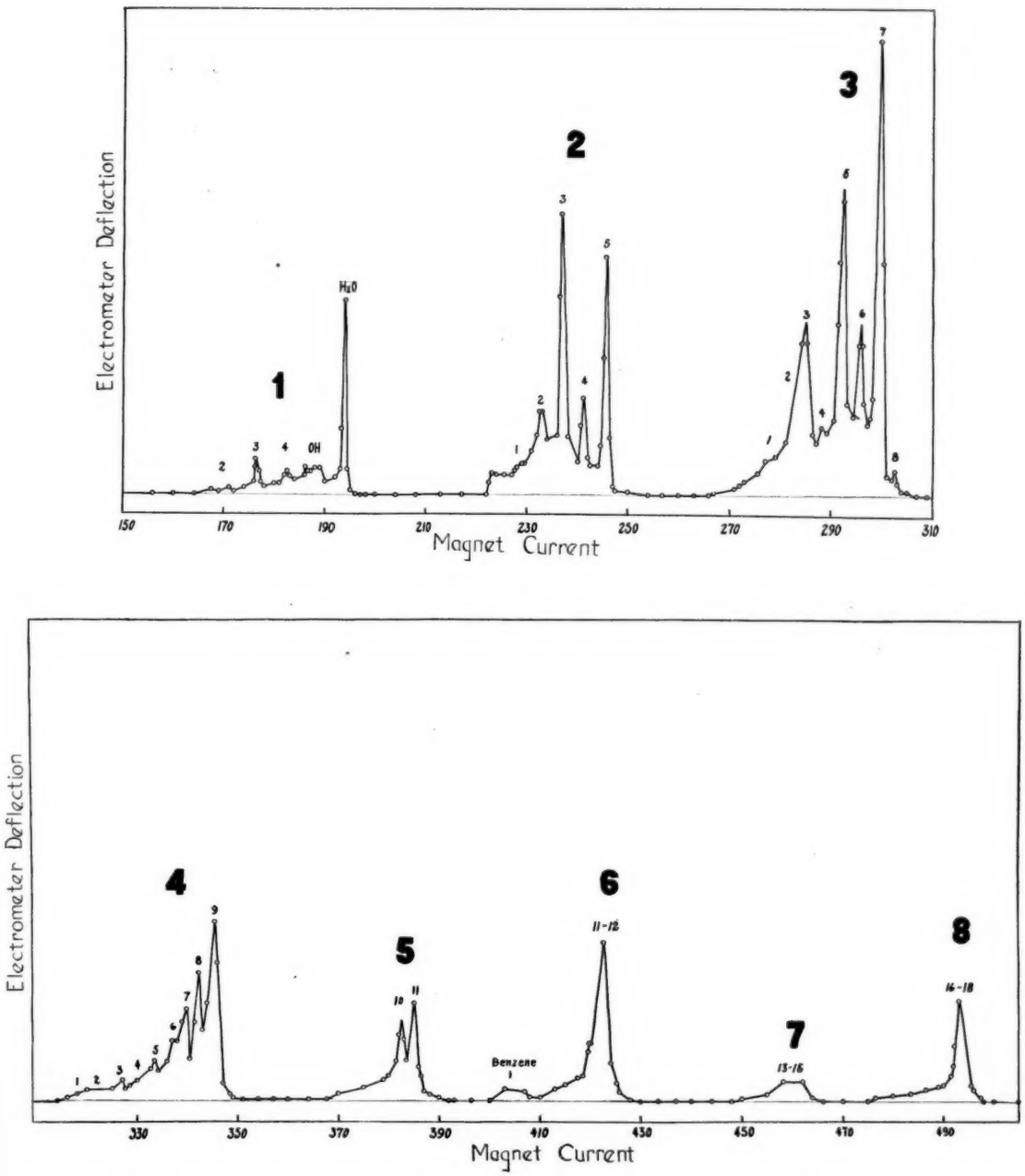


FIG. 1. The ions detected when *n*-octane is dissociated by electron impact. The large numerals give the numbers of carbon atoms and the small numerals the number of hydrogen atoms in the ions produced.

is that they permit an explanation of the variations in the peak heights.

The smallness and lack of structure of the peaks above $4C$ is rather surprising, and at first sight suggests that the result is spurious. Such an effect might occur due to differential absorption of these large ions in the magnet chamber. Their mean free path is of course shorter than that of the smaller ions and absorption should be greater for that reason. However, variation of the pressure produced no marked changes in the ratios of peak heights, as should be observed if differential absorption were playing a part. This can be seen from Table I, wherein ion percentages are given for various pressures. The pressures listed are those in the ionization chamber, but the pressure in the magnet chamber, although much smaller, of course varies simultaneously with the other.

It should be borne in mind that the mass scale in Fig. 1 is not linear and that the peaks corresponding to heavy ions therefore are not actually as small in width as they appear. This nonlinearity is corrected for in the data of Table I, and the percentages given there are true ion percentages.

Grateful acknowledgment is made to the Detroit Edison Company for the financial support of this research and for permission to publish the results.

Bond Energies and Mass Defects in Atomic Nuclei

W. M. LATIMER AND W. F. LIBBY, *Department of Chemistry, University of California*

(Received November 25, 1932)

The problem of the interpretation of the mass defect curve is discussed in reference to the coupling of protons and electrons proposed by Latimer. Gamow's equation is modified by making the attractive energies the sum of the bond energies. For certain symmetrical nuclei approximate values for the mass defect may be calculated which are in good agreement with the experimental results.

GAMOW[1] has suggested that the energy of a nucleus built up of alpha-particles may be represented by an equation of the form:

$$E = CN_\alpha - f(Z^2/R), \qquad (1)$$

where N_α is the number of alpha-particles, Z the charge on the nucleus, and R the radius. The first term postulates that the energy of attraction is proportional to the number of alpha-particles and the second term that the energy of repulsion is a function of the energy of the field produced by the charged nucleus.

It is obvious that such an expression is in qualitative agreement with the facts: with increasing values for N_α and Z, the mass defect curve at first increased but with higher atomic numbers the repulsive term becomes so large that the curve passes through a maximum and then decreases to such an extent that radioactive decomposition occurs. However, if one attempts to calculate from Eq. (1) a quantitative mass defect curve for the $4n$ proton series (i.e., the nuclei which may be considered as built up of alpha-particles and "cementing electrons"), it appears to be impossible to obtain agreement employing any reasonable assumptions regarding the energies of the extra electrons. Moreover, an inspection of the experimental values for the lighter elements of the series, shows that the increase in the mass defect is not regular. It is doubtless small for beryllium with 2 alpha-particles, larger for carbon with 3 particles, very much larger for oxygen and small again for the addition of the fifth alpha-particles to form neon.

We wish to discuss these problems in terms of the nuclear structure proposed by Latimer.[2] The essential feature of this theory is the close packing of alpha-particles in a tetrahedral pattern. Each alpha-particle is pictured as a small tetrahedron with a proton at each corner and the coupling pattern is such that the tetrahedral angle between protons is maintained throughout the structure. It may be of significance that this is the angle required for the addition of half unit spin vectors by the quantum mechanics. The extra or "cementing" electron pairs enter whenever four protons come together at a point. The structure thus gives a basis for the entrance of the first electron pair at argon, 40, the second pair at zinc, 68, and in general gives the correct number of alpha-particles and extra electrons. Moreover, it offers an explanation for the maxima in the abundance curve for the lighter elements and for the termination of the radioactive decomposition series at lead.

If we adopt the viewpoint of this theory we should modify Eq. (1) by assuming that the attractive energy is proportional, not to the number of alpha-particles, but to the number and kinds of *bonds* between the alpha-particles.

$$E = \Sigma \text{ bond energies} - f(Z^2/R). \qquad (2)$$

In the proposed structure for nuclei of the $4n$ proton type, there are but three kinds of bonds; those between 2 protons, between 3 protons and between 4 protons and an electron pair. Hence a knowledge of these three bond energies would permit a rough evaluation of the first term of this equation.

[1] Gamow, *Der Bau des Atomkerns und die Radioaktiv.*, p. 21. Hirzel, Leipzig, 1932.

[2] Latimer, J. Am. Chem. Soc. 53, 981 (1931).

The classical relativistic expression for the electromagnetic or field mass, $\frac{2}{3}Z^2/R$, assumes a uniform distribution of charge over a spherical shell. Now one of the interesting features of the proposed nuclear structure, is that the entrance of the extra electrons makes the interior of the lattice electrically neutral and the whole of the positive charge occurs on the surface of the

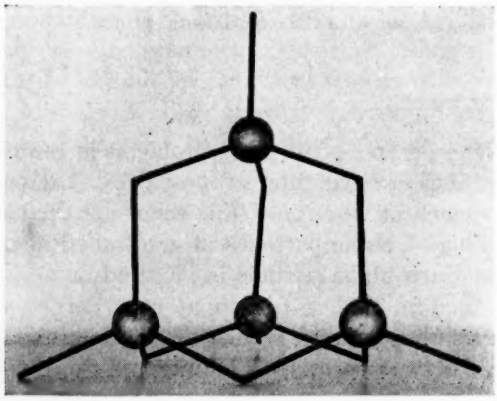


FIG. 1. Oxygen 16, four alpha-particles. Each alpha-particle is represented by a ball for the electron pair and four bars for the protons.

lattice. Moreover, the structures for O^{16} (see Fig. 1), A^{40}, Xe^{124}] (see Fig. 2), and Po^{208}, are not far from spherical symmetry. So in these special cases the classical expression may give at least an approximate value for the field energy.

For these nuclei, then, we may set up expressions for the mass defect, i.e., the energy of

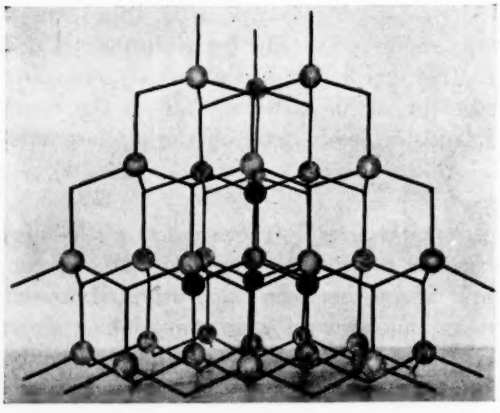


FIG. 2. Xenon 124, thirty-one alpha-particles and four extra electron pairs, which are represented by the black balls.

formation from alpha-particles and electrons, in the following manner. We will write for the energy of the alpha-particle,

$$E_\alpha = E_{\alpha'} - \tfrac{2}{3}(Z_\alpha^2/R_\alpha), \qquad (3)$$

where $E_{\alpha'}$ is the interaction energies of the four protons and two electrons. In oxygen, 16, we have 4 alpha-particles and 6 two-proton bonds, hence

$$E_0 = 4E_{\alpha'} + 6E_{2PB} - \tfrac{2}{3}(Z_0^2/R_0). \qquad (4)$$

Then from (3) and (4) we may express the mass defect of oxygen in terms of the energy of the bond and the charges and radii of the alpha-particle and oxygen nucleus.

$$MD_0 = 6E_{2PB} - \tfrac{2}{3}(Z_0^2/R_0) + 4x\tfrac{2}{3}(Z_\alpha^2/R_\alpha). \qquad (5)$$

For the heavier elements we will have similar expressions but these will contain also the energy of the three-proton bonds and the bond formed by 4 protons and a cementing electron pair. This latter has been represented in the models by a dark ball and we shall designate the energy of this bond as $E_{\alpha''}$.

In general then we have four parameters which must be determined, three-bond energies and the lattice constant which determines the radius. These parameters, however, are not all independent and our choice of values is confined to narrow limits by experimental facts. Thus Gamow[1] uses 2.2×10^{-13} cm as the radius of the alpha-particle. The effective value in the nuclear lattice may be slightly larger than for the free alpha-particle, but should give a calculated value for the radius of the lead nucleus (or Po^{208}), probably not greater than 8×10^{-13}. We have used 2.4×10^{-13} as the lattice value and calculate the radii given in Fig. 3. In these calculations we have taken the average distance of the surface protons from the center of the lattice. This of course is only an approximation but should give comparable values which are sufficient in view of the somewhat arbitrary choice of this parameter.

Aston's experimental value for the mass defect of the alpha-particle is 0.029 mass (atomic weight) units. It would seem that the value for $E_{\alpha''}$ should be somewhat less in view of the sharing of protons between two groups. The energy of the two-proton bond should be about

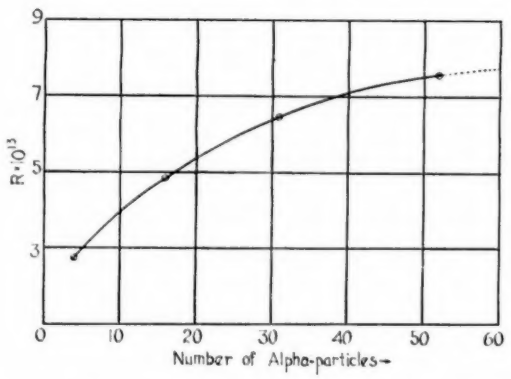


FIG. 3. Nuclear radius as a function of the number of alpha-particles.

one-third that of the three-proton bond and several considerations indicate that this in turn is less than $E_{\alpha''}$. The values which we have arbitrarily chosen to give the best agreement are $E_{2PB}=0.005$, $E_{3PB}=0.017$ and $E_{\alpha''}=0.020$, all expressed in mass units. The calculations are summarized in Table I.

Now while we do not attach any great importance to the quantitative agreement of the experimental and our calculated mass defects, we do believe it to be significant that the number and kinds of bonds in these structures are consistent with the reasonable values for the four parameters.

The assumption of the constancy of the $E_{\alpha'}$ value throughout all of the structures is doubtless not strictly true: especially is this so in the case of the one alpha-particle in xenon and the four alpha-particles in polonium which lie inside the lattice, and may therefore be considered as equivalent to the $E_{\alpha''}$. Subtracting the difference between 0.029 and 0.020 for these particles one obtains the mass defects given in brackets. It would seem that the value for E_{2PB} should be greater than one-third of E_{3PB}, but in view of the approximate nature of the calculations, the discrepancy is not important.

The large effect of the nuclear charge in the case of the heavier elements explains a number of anomalies in the abundance of these elements. Thus for the elements of even atomic number, the $4n-2$ proton type becomes more abundant than the $4n$ type which predominates with the lighter elements. This may be interpreted as meaning, that for large Z, the effect on the mass defect of reducing the charge by the removal of two protons, is much greater than the energy of

TABLE I. *Summary of calculations of mass defect.*

	$R\times10^{13}$	Bond energy	Δ Field energy	Mass defect Calculated	Mass defect Experimental*
O_{16}	2.75	$6\times0.005=0.030$	$0.0239-0.0068=0.017$	0.013	0.009
A_{40}	3.90	$9\times0.005=0.045$			
		$3\times0.017=0.051$			
		$1\times0.020=0.020$			
		0.116	$0.085-0.017=0.068$	0.048	0.050
Zn_{64}	4.86	$6\times0.005=0.030$			
		$12\times0.017=0.204$			
		$1\times0.020=0.020$			
		0.254	$0.189-0.027=0.162$	0.092	0.095
Xe_{124}	6.49	$12\times0.005=0.060$			
		$24\times0.017=0.408$			
		$4\times0.020=0.080$			
		0.548	$0.460-0.053=0.407$	0.141 (0.132)	0.133
Po_{208}	7.56	$18\times0.005=0.090$			
		$40\times0.017=0.680$			
		$10\times0.020=0.200$			
		0.970	$0.958-0.089=0.869$	0.101 (0.065)	<0.095

* Aston's values as tabulated by Gamow.[1] The value for Po^{208} should be less than that for Pb^{208} which is 0.095, since the former is unstable with respect to the latter.

binding these two protons. Hence Po^{208} which one would expect to be abundant from the symmetry of the lattice model, is unstable with respect to the loss of two protons to give Pb^{206}, and also in this case to the addition of an extra electron pair to give Pb^{208}.

The effect of the charge explains also why Xe^{124}, adds an alpha-particle and electron pair to the face of its structure to form Xe^{128} rather than simply an alpha-particle to a corner to form Ba^{128}. The first process gives no change in field energy and an increase of 0.003 in bond energy ($E_{\alpha''}-E_{3PB}$). The second process gives an increase of $3E_{2PB}$ or 0.015 mass units in bond energy but the effect of the increase in charge is -0.035 mass units, or a net energy of 0.020 mass units against the reaction. Aston's value for the difference in mass defect for Xe^{124}, and Xe^{128}, is 0.004 units in agreement with the 0.003 which we calculate.

As another point of some interest, we may calculate the total energy evolved in the radioactive decomposition of uranium into lead. Uranium has eight alpha-particles and three electron pairs more than lead and we postulate that these form the most stable bonded group on the surface of the lead structure. Then using the extrapolated value for the radius of uranium, Fig. 3, and the same bond energies as before, we calculate 0.052 mass units for the total change, as compared with 0.048 units given by Rutherford and Chadwick,[3] as the best calorimetric value.

With the exception of oxygen, 16, the lighter elements are too unsymmetrical to attempt an evaluation of the field energy. However, the irregular increase in the mass defect is roughly proportional to the number of two-proton bonds which the theory indicates, and is added confirmation, we believe, of the point of view which we have presented.

[3] Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, p. 163, MacMillan, 1930.

Some Thermodynamic Properties of the H^1H^2, H^2H^2 Molecules and Compounds Containing the H^2 Atom

HAROLD C. UREY AND D. RITTENBERG, *Chemical Laboratory of Columbia University*

(Received October 4, 1932)

The summations of state and free energies of the molecules H_2^1, H_2^2 and H^1H^2 have been calculated at temperatures from 20.4 to 700°K and their dependence on the spin and statistics of H^2 discussed and illustrated. The equilibrium constants of the reaction $H_2^1+H_2^2=2\,H^1H^2$ are found to deviate markedly from the value 4 expected from simple probability considerations. The equilibrium constants of the reactions $H_2^1+2\,H^2Cl \rightleftharpoons H_2^2+2\,H^1Cl$ and $H_2^1+2\,H^2I \rightarrow H_2^2+2\,H^1I$ have been calculated and found to be appreciably different from unity, showing that appreciable differences in equilibrium constants of chemical reactions may be expected depending on which isotope of hydrogen enters into the reaction. Small differences in the electrode potentials of the two hydrogen isotopes may be expected but no exact estimates have been made.

THE application of statistical methods to the calculation of thermodynamic properties of gases has been understood for many years, though the assignment of the proper statistical weights to the degenerate energy levels was only possible after the discovery of the electron spin, nuclear spin and the quantum mechanics. With this correct assignment and the detailed data of molecular spectra available, the calculation of the heat capacity, entropy, energy, and free energy of diatomic molecules was immediately possible. The careful researches of Giauque and his co-workers[1] especially have shown that entire confidence can be placed in the results of such calculations. As a result, it is possible to predict many properties of H^2,[2] and its compounds by the application of statistical mechanics and the known molecular spectrum of H_2^1 and its compounds though this isotope has not as yet been secured in sufficiently high concentrations to make measurements possible. It is the purpose of this paper to report the results of our calculations at this time, limiting our calculations for the most part to those quantities that are independent of the nuclear spin of H^2 and whether the symmetric or antisymmetric states occur. Thus no heat capacities at low temperatures on entropies have been calculated at this time. Experiments are in progress in this laboratory looking to the experimental verification of the theoretical calculations.

The Methods of Calculating the Free Energy

The standard free energy of a diatomic molecule is given by the equation,[3]

$$F^0 = Mc^2 - (3/2)RT \ln M - (5/2)RT \ln T + RT \ln P + 7.2646T - RT \ln Q' \quad (1)$$

where Mc^2 is all the energy of the molecule at absolute zero except the zero point energy due to molecular vibration, and $Q'=\Sigma p \exp(-E/kT)$, and all the other symbols have their usual meaning. Since the term Mc^2 does not concern us it may be ignored. The statistical weight, p, is equal to $2J+1$ multiplied by a factor which depends on the nuclear spin. If the nuclei are not identical, and the electronic state is E^+_g as in the case of H_2, HCl and HI, this factor is $(2i_1+1)\times(2i_2+1)$ the i_1 and i_2 being the nuclear spins. If the nuclei are identical, then this factor is $(2i+1)(i+1)$ for the even values of J and $(2i+1)i$ for the odd levels, if the nuclei follow the Bose-Einstein statistics, and if the Fermi-Dirac statistics, the factors are $(2i+1)i$ and $(2i+1)\times(i+1)$ for the even and odd levels, respectively.

[1] W. F. Giauque and Roy Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932). J. O. Clayton and W. F. Giauque, ibid. **54**, 2610 (1932); W. F. Giauque, ibid. **52**, 4816 (1930); W. F. Giauque and H. L. Johnston, ibid. **50**, 3221 (1928).

[2] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. [2], **40**, 1; **39**, 164 (1932); see also Walker Bleakney, Phys. Rev. [2], **41**, 32 (1932).

[3] An excellent summary of the relation between heat capacities, free energies, and energies and the summation of state has been given by Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

The energy, E, follows a formula of the form,[4]

$$E/hc=\tilde{\omega}_e(v+1/2)-x\tilde{\omega}_e(v+1/2)^2+[B_e-\alpha(v+1/2)+\gamma(v+1/2)^2-\delta(v+1/2)^3]J(J+1)$$
$$+[D_e+\beta(v+1/2)]J^2(J+1)^2+F_eJ^3(J+1)^3. \quad (2)$$

The zero point energy is then,

$$E_0^0/hc=(\tfrac{1}{2}\tilde{\omega}_e-\tfrac{1}{4}x\tilde{\omega}_e)N, \quad (3)$$

(N=Avogadro number) and it is convenient to remove this energy from the expression for Q', so that $\ln Q'=E_0^0/kT+\ln\Sigma pe^{-E/kT}$ where E now contains all the terms of (2) except those of E_0^0 as here given by the Eq. (3).[5] This separation has the advantage that the zero point energy is an additive term in the free energy and need not be considered again in the summations. The new summation of state now becomes,

$$Q=\sum p\exp -E/kT. \quad (4)$$

This gives results equivalent to those secured by previous authors.

Mulholland[6] has given a rapidly converging series for this summation insofar as it depends on the exponential term containing $J(J+1)$ and Giauque and Overstreet[7] have extended the work to include higher terms in $J^2(J+1)^2$. The resulting formula is

$$Q=\sum Q_v=\sum_v\left[\frac{kT}{B_vhc}+\frac{1}{12}+\frac{7}{480}\frac{B_vhc}{kT}-\frac{2D_v}{B_v}\left(\frac{kT}{B_vhc}\right)^2\right]\exp\frac{hc}{kT}\left[\frac{B_v}{4}+\frac{D_v}{16}-\tilde{\omega}_ev+x\tilde{\omega}_ev(v+1)\right]. \quad (5)$$

This formula can be used for calculating the free energy if $T/B_v\geqq 4$ (approximately), but if used to calculate the heat capacity will give incorrect results unless the heat capacity has reached nearly classical values. It does not include the contribution of the nuclear spins to the *a priori* probabilities; to include the contribution of these spins, it is necessary to add a term to the free energy, $-RT\ln(2i_1+1)(2i_2+1)$, i_1 and i_2 being the spins of the two nuclei, if the nuclei are unlike and $-RT\ln[(2i+1)^2/2]$ if the nuclei are identical. The formula cannot be used in the cases of H^1H^2, H^1H^1, and H^2H^2 at temperatures below about 298.1°K, since it holds only in the region where $\Sigma(2J+1)\exp(-E/kT)$ over the even values of J is equal to this summation over odd values of J.

The H^1H^2 and H_2^2 Molecules

The atomic weights of H^1 and H^2 relative to O^{16} as 16.0000 are 1.00778[8] and 2.01353.[9] With Mecke and Childs'[10] values for the relative abundancies of the oxygen isotopes, the values corrected to the chemical scale are 1.00756 and 2.01309. The reduced masses of the molecules H_2^1, H^1H^2 and H_2^2 in atomic weight units are: 0.50378, 0.67148, and 1.00654 and the ratios of these needed to calculate the energy level formulae are:

$$\rho_{12}=(\mu_{11}/\mu_{12})^{1/2}=0.86617$$
$$\rho_{22}=(\mu_{11}/\mu_{22})^{1/2}=0.70746. \quad (6)$$

Birge, Jeppesen and Hyman[11] discussed the energy levels of hydrogen. The $\Delta G(1/2)$ value is larger than is to be expected by using a smooth formula derived from the remaining ΔG's. Also

[4] We use $J(J+1)$ instead of the usual $(J+\frac{1}{2})^2$ because the former has the better theoretical support. (Private communication from J. L. Dunham.) In most cases no appreciable difference is encountered due to the use of one or the other. In our problem an important difference arises for the latter form gives a zero point rotational energy of $\frac{1}{4}Bhc$ which in the case of H_2^1 amounts to about 42 calories per mole, which is not negligible at all.

[5] E_0^0, as here defined differs from that used by Giauque and his co-workers. These authors use E_0^0 to include the zero point vibrational energy, the Mc^2 term mentioned above and also rotational zero point energy. We assume the rotational zero point energy to be zero and ignore the Mc^2 term since it does not concern us. M is the rest mass in the hypothetical vibrationless state.

[6] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928).

[7] W. F. Giauque and Roy Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[8] F. W. Aston, Proc. Roy. Soc. **A115**, 487 (1927).

[9] K. T. Bainbridge, Phys. Rev. [2], **41**, 115 (1932).

[10] R. Mecke and W. H. Childs, Physik **68**, 362 (1931).

[11] R. T. Birge, H. H. Hyman and C. R. Jeppesen, Nature **123**, 277 and 462 (1930); H. H. Hyman, Phys. Rev. **36**, 187 (1930).

the $B_0(=59.331)$ is somewhat irregular since it cannot be calculated from a formula derived from the higher B_v values. These authors regard these irregularities as a perturbation, though it is difficult to understand what can possibly perturb the normal state of the hydrogen molecule. They give a formula for the higher energy levels and advise its use for most purposes. Unfortunately it is the lowest levels that are of interest to us here. The question arises as to whether these irregularities would be present in the H^1H^2 and H_2^2 molecules as well, a question which probably cannot be answered experimentally for some time. Therefore, we have made these calculations assuming two energy level formulae for the hydrogen molecule, (1) the smooth formula of Birge, Jeppesen and Hyman, and (2) a formula derived from the data on the first three vibration levels of the molecule, but which will not fit the higher levels. We believe the latter formula to be better for our purposes. A comparison of the results from the two formulae enables us to estimate our possible error due to this uncertainty.

The molecular constants of the H_2^1 and H^1H^2 and H_2^2 molecules with the Birge-Jeppesen-Hyman formula for H_2^1 referred to as I and with our formula covering the lower vibrational levels only referred to as II are given in Table I.

TABLE I.

	I		
	H_2^1	H^1H^2	H_2^2
$\tilde{\omega}_e$	4371	3786.0	3092.3
$x\tilde{\omega}_e$	113.5	85.2	56.8
B_e	60.564	45.439	30.312
α	2.7931	1.8151	0.98898
γ	0.0105	0.00591	0.00263
δ	0.002406	0.001173	0.000426
$-D_e$	0.0465	0.0262	0.0116
β	1.35×10^{-3}	6.58×10^{-4}	2.39×10^{-4}
F_e	5.18×10^{-5}	2.19×10^{-5}	0.649×10^{-5}

	II		
	H_2^1	H^1H^2	H_2^2
$\tilde{\omega}_e$	4403	3813.75	3114.95
$x\tilde{\omega}_e$	120.5	90.4	60.3
B_e	60.871	45.670	30.466
α	3.124	2.0302	1.106
γ	0.0875	0.0493	0.0219
δ	—	—	—
$-D_e$	0.0465	0.0262	0.0116
β	1.35×10^{-3}	6.58×10^{-4}	2.39×10^{-4}
F_e	5.18×10^{-5}	2.18×10^{-5}	0.649×10^{-5}

The zero point energies of the three molecules in calories per mole are:

	H_2^1	H^1H^2	H_2^2
I	6133.8	5323.1	4356.9
II	6175.5	5358.9	4386.6

Since the known spins of nuclei are observed to be integral if the atomic weight is even, and half integral if it is odd, we may expect that the H^2 will have a spin of 0 or 1. Also since nuclei of even atomic weight will follow the Bose-Einstein statistics and those of odd atomic weight the Fermi-Dirac statistics, we expect that H^2 will follow the former. Thus N^{14}, which may be regarded as a C^{12} nucleus plus the fundamental particles present in the H^2 nucleus, has an integral spin and the wave functions symmetric in the nuclei are observed. We may expect that the rotational states with even J will be present, if $i_2=0$, and have a higher *a priori* probability than those with odd J, if $i_2=1$. We have considered these two values of the spin and also the difference due to the two possible statistics, Bose-Einstein and Fermi-Dirac. At the higher temperatures considered, the equilibrium constants are independent of the statistics and spin, but at lower temperatures this is not the case.

The results of the calculations are listed in Table II. The temperatures for which calculations have been made have been selected because of the possibility of checking the results experimentally in various ways in the neighborhood of these temperatures.

The equilibrium constant for the reaction

$$H^1H^1+H^2H^2\rightarrow 2\,H^1H^2 \tag{7}$$

can be calculated with the results of the previous tables, though it is given more directly by the equation

$$-RT\ln K=\Delta F^0=\Delta E_0^0 - \frac{3}{2}RT\ln\frac{M_{12}^2}{M_{11}M_{22}} - RT\ln\frac{Q_{12}^2}{Q_{11}Q_{22}}. \tag{8}$$

The equation also permits one to see how the uncertainty of energy levels affects K. Since the Q's are approximately inversely proportional to the B_0's, and the B_0's of the three molecules are nearly proportional to each other, the errors cancel largely and K is independent of the un-

TABLE II. *Thermodynamic constants of H_2^1, H^1H^2, H_2^2. Formula II was used in these calculations.*[4]

	H_2^1, $i=1/2$, F.-D.			H^1H^2, $i=1/2$, $i_2=0$[2]			H_2^2, $i_2=0$, B.-E.[3]			H_2^2, $i_2=0$, F.-D.[3]		
T	Q	$-\frac{F^0-E_0^0}{T}$	F^0	Q	$-\frac{F^0-E_0^0}{T}$	F^0	Q_e	$-\frac{F^0-E_0^0}{T}$	F^0	Q_0	$-\frac{F^0-E_0^0}{T}$	F^0
50	1.303	14.776	+ 5436.7	2.471	17.253	+ 4496.2	1.029	16.370	3568.1	0.540	15.089	3632.1
100	2.682	19.652	+ 4210.3	3.897	21.601	+ 3198.9	1.385	20.402	2346.4	1.314	20.298	2356.8
200	5.390	24.481	+ 1279.3	6.986	26.202	+ 118.5	2.514	25.028	− 619.0	2.513	25.028	618.9
298.1	7.764	27.187[1]	− 1929.1	10.072	28.911	− 3259.4	3.665	27.759	− 3888.3	3.665	27.759	− 3888.3
400	10.185	29.187[1]	− 5499.3	13.291	30.922	− 7009.9	4.866	29.782	− 7526.3	4.866	29.782	− 7526.3
575	14.371	31.673	−12036.6	18.857	33.419	−13857.0	6.940	32.290	−14179.9	6.940	32.290	−14179.9
700	17.387	33.028[1]	−16944.4	22.854	34.778	− 1895.6	8.431	33.653	−19170.5	8.431	33.653	−19170.5

[1] These agree with Giauque's values when account is taken of the different value of R used. Throughout we have used the values of the natural constants given by R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).

[2] To secure values for other values of i_2, multiply the Q's as given by $(2i_2+1)$, add $-R\ln(2i_2+1)$ to $(F^0-E_0^0)/T$ and $-RT\ln(2i_2+1)$ to F^0.

[3] The values of the Q, $(F^0-E_0^0)/T$, and F^0 for H_2^2 for any other value of i_2 can be secured from the values of Q_e and Q_0 which are the summations over the even and odd levels respectively. Thus the Q by using the Bose-Einstein statistics is $Q=(2i_2+1)(i_2+1)Q_e+(2i_2+1)i_2Q_0$, and by using the Fermi-Dirac is $Q=(2i_2+1)i_2Q_e+(2i_2+1)(i_2+1)Q_0$, and the corresponding values of $(F^0-E_0^0)/T$ can be calculated from the tabulated values by adding $R\ln Q_e$ to and subtracting $R\ln Q$ from the values $F^0-E_0^0/T$ given under (H_2^2, $i_2=0$, B.-E.) and those of F_0 by adding $RT\ln Q_e$ to and subtracting $RT\ln Q$ from the F^0 values given under the same heading.

[4] If formula (I) is used instead of formula (II) the Q's are increased by about one part in 600 decreasing F^0 by about 2.7 calories at 700°K. A more important change is made in F^0 by the change in zero point energy. The F^0 values of H_2^1 must be decreased by 41.7 calories, those of H^1H^2 by 35.8 calories and those of H_2^2 by 29.7 calories, if formula (I) is used.

certainty in the B_0's of the three molecules, unless only part of them are irregular. The effect of the uncertainty in the zero point energy is greater, but amounts to only 1.4 percent of K at the lowest temperature and the uncertainty at higher temperatures is less. The total error in these values of K can hardly be greater than this.

The values of the equilibrium constants are given in Table IIIA. A marked deviation from the classical value of 4 is evident over the entire range and becomes very great at low temperatures. The equilibrium constants are independent of i_2 and the statistics of the H^2 nucleus at temperatures above 200°K.

It is of interest to consider the equilibrium constants at some temperature at which they are appreciably affected by the spin and statistics of the H^2 nuclei. Such a temperature is that of liquid hydrogen, 20.4°K. The values of the Q's of the H^1H^1, H^1H^2 and H^2H^2 molecules at this temperature if $i_1=1/2$ and $i_2=0$ are: $Q(H^1H^1)=1.022$; $Q(H^1H^2)=2.0114$; $Q_e(H^2H^2$, Bose-Einstein$)=1.0000$; $Q_0(H^2H^2$, Fermi-Dirac$)=0.04485$.[12] The equilibrium constants calculated, assuming that i_2 may be 0, 1/2, 1, or 3/2 and that the nuclei may follow either the Bose-Einstein or Fermi-Dirac statistics, are given in Table IIIB.

With these constants it is possible to calculate the ratios of the number of molecules of one variety to that of another variety. Such ratios

[12] See footnotes to Table II for the method to be used in securing the Q's for other values of i_2.

TABLE IIIA.

	Bose-Einstein statistics		*Fermi-Dirac statistics*	
T	$-\Delta F^0$	K	$-\Delta F^0$	K
		$i_2=0$		
50	12.3	1.132	76.4	2.157
100	159.0	2.227	169.4	2.346
200	423.4	2.903	423.5	2.904
298.1	701.4	3.269	701.4	3.269
400	994.1	3.494	994.1	3.494
575	1497.5	3.710	1497.5	3.710
700	1856.2	3.800	1856.2	3.800
		$i_2=1$		
	The constants are independent of spin above 200°K.			
50	29.4	1.345	50.3	1.659
100	162.4	2.265	165.9	2.311
200	423.5	2.903	423.5	2.903

TABLE IIIB.

i_2	K(B.-E.)	K(F.-D.)
0	0.1032	2.302
1/2	0.1356	0.3640
1	0.1515	0.2842
3/2	0.1609	0.2562

TABLE IIIC.

	i_2	$(H_2^1)/(H^1H^2)$	$(H_2^1)/(H_2^2)$	$(H^1H^2)/(H_2^2)$
B.-E.	0	63.99	422.7	6.606
	1/2	60.97	504.2	8.269
	1	59.91	543.6	9.074
	3/2	59.37	567.0	9.550
F.-D.	3/2	55.91	800.8	14.32
	1	55.30	869.1	15.72
	1/2	54.03	1063.	19.67
	0	49.86	5719.	114.7

are given in Table IIIC for a sample of hydrogen containing 1 atomic percent of H^2. These ratios are sufficiently different to make possible the determination of the spin and statistics of H^2 by any method which can determine the relative numbers of the three types of molecules in a sample of hydrogen which has been brought to equilibrium at 20.4°K. It seems that this equilibrium would be established under the same conditions as those necessary for the ortho-para equilibrium of the H_2^1 molecule. Also it does not seem likely that this equilibrium will be established more rapidly than the ortho-para equilibrium. If these assumptions prove to be true, it should be possible to prepare a sample of hydrogen having the relative numbers of the three molecules characteristic of the equilibrium at 20.4°K and to hold it at ordinary temperatures for a time sufficient to determine the relative numbers of the molecules by a magnetic deflection of ions such as that used by Bleakney.[13] This appears to us as a most promising method for securing the spin and statistics of H^2 with concentrations of H^2 now available.

At the temperatures considered here, the nuclear spins have no influence on the numerical values.

The quantities, Q, $-(F^0-E_0^0)/T$, and F^0 at temperatures from 200° to 700° are listed in Table IV. The spin of Cl^{35} is taken as zero since it does not affect the observable quantities.

The ratio of the equilibrium constants, K_1 and K_2, of the reactions (11) and (12) respectively, and the free energy change in reaction (13) are given in Table V.

[13] W. Bleakney, Phys. Rev. [2], **41**, 32 (1932).

THE FREE ENERGY OF H^2Cl

Giauque and Overstreet have given tables of $F^0-E_0^0/T$ for H^1Cl and for Cl_2^{35}, Cl_2^{37}, and $Cl^{35}Cl^{37}$. They have used the atomic weight of natural hydrogen as the atomic weight of H^1, but this makes only a slight difference in the results. The energy levels of the H^1Cl^{35} molecule are given by the formula,[14]

$$E/hc=2989.68(v+1/2)-51.90(v+1/2)^2 +(10.585-0.3062(v+1/2) +0.0016(v+1/2)^2)J(J+1) -5.0\times10^{-4}J^2(J+1)^2. \quad (9)$$

The energy levels of the H^2Cl^{35} molecule become

$$E/hc=2144.44(v+1/2)-26.70(v+1/2) +(5.4459-0.1130(v+1/2)+0.00042 (v+1/2)^2)J(J+1)-1.3 \times10^{-4}J^2(J+1)^2. \quad (10)$$

The zero point energies of H^1Cl^{35} and H^2Cl^{35} are 4214.4 and 3030.4 calories per mole respectively.

We are particularly interested in the ratio of the equilibrium constants of the two reactions:

$$H_2^1+Cl_2^{35}\rightarrow 2\ H^1Cl^{35}, \quad (11)$$

$$H_2^2+Cl_2^{35}\rightarrow 2\ H^2Cl^{35}. \quad (12)$$

Subtracting these pairs of reactions, we secure

$$H_2^1+2\ H^2Cl^{35}=H_2^2+2\ H^1Cl^{35}, \quad (13)$$

and the equilibrium constant of this reaction is the ratio of the equilibrium constants of the reactions (11) and (12). The ratio of equilibrium constants is given by the equation:

$$-RT\ln\frac{K_1}{K_2}=\Delta E_0^0-\frac{3}{2}RT\ln\frac{M^2_{H^1Cl}M_{H_2^2}}{M^2_{H^2Cl}M_{H_2^1}}-RT\ln\frac{Q^2_{H^1Cl}Q_{H_2^2}}{Q^2_{H^2Cl}Q_{H_2^1}}. \quad (14)$$

THE FREE ENERGY OF H^2I

The energy levels of hydrogen iodide are not well known. Czerny has observed the rotation bands from which the B_0 and D_0 can be secured. The values of the vibrational constants $\tilde{\omega}_e$ and

[14] This equation is taken from the recent paper of Meyer and Levin (Phys. Rev. **34**, 44 (1929) and Colby (ibid. 53 (1929)) and differs slightly from that used by Giauque and Overstreet. Only negligible errors are introduced by the change in rotational constants, though the zero point energies are changed by a few calories.

TABLE IV.

	H^1Cl^{35}, $i_1=1/2$			H^2Cl^{35}, $i_2=0$		
T	Q	$-(F^0-E_0^0)/T$	F^0	Q	$-(F^0-E_0^0)/T$	F^0
200	27.493	36.306	− 3046.8	26.287	36.299	− 4229.3
298.1	40.666	39.065*	− 7431.0	39.001	39.064	− 8614.7
400	54.375	41.103*	−12226.6	52.331	41.109	−13413.0
575	78.013	43.622	−20868.1	75.532	43.640	−22062.4
700	95.083	44.992*	−27279.9	92.722	45.024	−28486.3

* These values agree with those of Giauque and Overstreet when account is taken of the spin of H^1 the slightly different energy formula used and the different value of R used.

TABLE V.

	$H_2^1+2\ H^2Cl^{35} \rightleftarrows H_2^2+2\ H^1Cl^{35}$					
T	0	200	298.1	400	575	700
ΔF	579.1	466.8	408.2	345.8	245.1	186.7
K_1/K_2	0.000	0.309	0.502	0.647	0.807	0.874

$x\tilde{\omega}_e$ are less certainly known. Czerny[15] reports a value of 2270 cm^{-1} for the $\Delta G(1/2)$ of this molecule which is also the value secured from the relation $\tilde{\omega}_e=2B^{3/2}/D^{1/2}$. Salant and Sandow[16] have secured 2233 cm^{-1} for the $\Delta G(1/2)$ of gaseous HI. Further work by Kirkpatrick[17] on the $v'=2\rightarrow v''=0$ infrared band gives approximately the following values for $\tilde{\omega}_0$ and $x\tilde{\omega}_0$; $\tilde{\omega}_0=2299$, $x\tilde{\omega}_0=33$. These latter values have been used in these calculations. The α-constant is unknown, but its neglect introduces but small errors. We take as the formula for the energy levels of H^1I

$$E=2299(v+1/2)-33(v+1/2)^2+6.420J(J+1)-0.000205J^2(J+1)^2, \quad (15)$$

and for the energy levels of H^2I,

$$E=1632.8(v+1/2)-16.6(v+1/2)^2+3.2385J(J+1)-0.0000522J^2(J+1)^2. \quad (16)$$

The zero point energies of H^1I and H^2I are 3245.7 and 2310.0 calories per mole, respectively.

The quantities for H^1I and H^2I are calculated for temperatures from 298.1° to 700°K since experimental tests of the theory are possible for this region. The results are given in Table VI.

The ratio of the equilibrium constants of the reactions,

$$H_2^1+I_2 \rightleftarrows 2\ H^1I \quad (17)$$

and

$$H_2^2+I_2 \rightleftarrows 2\ H^2I \quad (18)$$

TABLE VI.

	H^1I, $i_1=1/2$			H^2I, $i_2=0$		
T	Q	$-(F^0-E_0^0)/T$	$+F^0$	Q	$-(F^0-E_0^0)/T$	F^0
298.1	65.670	43.797	− 9810.2	64.786	43.793	−10744.7
400	87.973	45.838	−15089.5	87.097	45.841	−16026.4
575	126.722	48.365	−24564.3	127.034	48.393	−25516.0
700	155.218	49.745	−31575.8	157.674	49.799	−32549.4

is again equal to the equilibrium constant of the reaction,

$$H_2^1+2\ H^2I \rightleftarrows H_2^2+2\ H^1I \quad (19)$$

and can be calculated as in the case of the analogous reactions involving hydrogen chloride. The calculated values of K_1/K_2 for the hydrogen and iodine, hydrogen iodide reactions are given in Table VII.

The use of formula (1) for the hydrogen levels changes K_1/K_2 by $10^{-2.43/T}$, which amounts to a decrease of 1.9 percent at 298.1° and 0.8 percent at 700°K. A change of 10 cm^{-1} in the $x\tilde{\omega}_e$ of HI changes these constants by the factor $10^{2.17/T}$ which is 1.7 percent at 298.1° and 0.7 percent at

TABLE VII.

T°K	0	298.1	400	575	700
$-F$	−82.46	90.1	153.1	239.9	278.9
K_1/K_2	0.0	1.164	1.212	1.234	1.222

[15] M. Czerny, Zeits. f. Physik **44**, 235 (1927).
[16] E. O. Salant and A. Sandow, Phys. Rev. **37**, 373 (1931).
[17] Private communication.

700°K. Finally we may estimate the effect of the use of $J(J+1)$ instead of $(J+1/2)^2$ in our equations. The use of the latter dependence on J would increase these constants by $10^{3.67/T}$ which amounts to 2.6 percent at 298.1° and 1.2 percent at 700°.

The ratio of K_1/K_2 of the H^1Cl and H^2Cl reactions is thus quite different from that of the H^1I and H^2I reactions. This difference is due to the difference in zero point energies largely; this energy difference in the case of reaction (13) is 579.1 calories and in that of reaction (19) is 82.46 calories. The term of Eq. (14) containing the masses is largely cancelled by that containing the Q's, so that the zero point energy is relatively important.

The ratio K_1/K_2 of the H^1I and H^2I reactions is sufficiently large at 575–700°K to permit test of these calculations, if rather high concentrations of H_2^2 can be secured. In any such sample the molecules H_2^1, H^1H^2 and H_2^2 must all be present. The concentration of H^1H^2 is determined by Eq. (8) and the calculated values of Table II, and thus for a sample containing a given ratio of H^1 to H^2 the concentration of hydrogen, hydrogen iodide and iodine can be calculated and compared with experiment.

The reactions (11) and (12) cannot be investigated readily since the equilibria are so far toward the hydrogen chloride side, but reaction (13) can probably be studied, if sufficiently high concentrations of H^2 can be secured. The various methods developed for concentrating H^2 are so promising that we believe that such tests of the theoretical calculations will be possible.

The Electrode Potentials of H_2^1 and H_2^2

The free energy change of the reaction between hydrogen and chlorine in an electrolytic cell differs from that considered above by the free energy of solution of gaseous hydrogen chloride in a water solution at the concentration used in the cell. Thus differences in the free energy of solution of H^1Cl and H^2Cl molecules, i.e., the solubilities of these two hydrogen chloride molecules, may exist and thus no prediction of electrode potentials can be made. It seems, though, that the free energy differences calculated above for these hydrogen-hydrogen halide reactions should give the order of magnitude of the electrode potential differences. These electrode potential differences at 298.1° are 0.00886 and 0.00195 volts in the cases of the hydrogen chloride and hydrogen iodide reactions respectively.

These differences are so small that no separation of the hydrogen isotopes can be expected by fractional electrolysis insofar as this fractionation depends on the differences of electrode potentials. The discovery by Washburne and Urey[18] that such fractionation does occur in commercial hydrogen-oxygen electrolytic cells with KOH solutions as electrolyte and nickel electrodes is probably due to other causes than the electrode potential differences, perhaps the rates of diffusion to the electrode surface or the rates of recombination of hydrogen atoms on the electrodes.

Though these calculations have not been experimentally confirmed, they are based on well established methods. They show that rather appreciable differences in thermodynamic properties of the compounds of H^1 and H^2 are to be expected. The differences of the vapor pressures of H_2^1 and H^1H^2 required by thermodynamic reasoning previously presented and demonstrated by Urey, Brickwedde and Murphy[2] is another marked variation in properties due to the large ratio of masses of the two isotopes of hydrogen. These differences as well as differences in reaction velocities, of which the electrolytic fractionation of the hydrogen isotopes is probably an example, are so great that had the abundance of H^2 been about equal to that of H^1, very marked variations of the atomic weight of hydrogen would certainly have been observed many years ago, with a considerable change in the historical development of chemistry.

[18] E. W. Washburne and H. C. Urey, Proc. Nat. Acad. Sci. **18**, 496–498 (1932).

Zeeman Effect in Solids

F. H. SPEDDING,[1] *Department of Chemistry, University of California*

(Received November 16, 1932)

The transverse Zeeman effect on the absorption lines of the monoclinic $GdCl_3 \cdot 6H_2O$ was examined at various field strengths. Photographs were made with the crystals at various temperatures. Enlarged reproductions and microphotometer curves are given. The results are discussed and explained on the assumption that if an electron is excited as a first approximation only its spin can orient in a magnetic field.

RECENTLY considerable interest has developed in the nature of energy states in solids and several theoretical papers have appeared which deal either directly or indirectly with the subject. Unfortunately the experimental evidence in this field is very meager so that the theorist has been greatly handicapped by the lack of facts upon which to build and check his theories. For this reason it was thought advisable at this time to report in some detail the progress made in experiments on the Zeeman effect in solids which are being carried out in this laboratory, even though the experiments will not be fully completed for some time.

Hund,[2] from rules of spectra, predicted the basic levels of the gaseous rare earth ions and then calculated their magnetic moments. As data on the gaseous ions were lacking he compared his results with those on solids and obtained excellent agreement with the experimental results. On the other hand, he obtained very poor agreement with ions of the iron group. If one examines the electronic structure of the two types of ions one can see why this might be true. In the case of the iron group the "active" or "magnetic" electrons are outside the kernel where they are subjected to the strong electric fields of the neighboring ions, while in the case of the rare earths the active electrons are in the $4f$ shell which is strongly shielded by the completed $5s$ $5p$ shells from the action of the neighboring ions.

Kamerlingh Onnes[3] and his associates have measured the magnetic susceptibility of the gadolinium ion in both the monoclinic $Gd_2(SO_4)_3 \cdot 8H_2O$ and the hexagonal $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$ over a temperature range of from 1.3°A to room temperature, and Giauque[4] has shown that the ${}^8S_{7/2}$ level predicted by Hund is in good agreement with the results over the entire range. He has also shown that the action of the crystalline electric fields on this level must be very small as the magnetic behavior is just what one would expect for the case of the free or gaseous ion.[5]

The absorption spectra of the gadolinium ions must therefore consist of lines which arise from transitions between this basic level (all S levels are single in the absence of fields) and various excited levels and the position of these lines will be effectively an energy level diagram of the excited states. These lines occur in multiplets, the positions of which are approximately the same for all gadolinium compounds examined. The numbers and position of the lines, however, within the multiplets, as Spedding and Nutting[6] have shown, change greatly with the various compounds and depend to a large extent on the crystalline symmetry of the compound, the higher the symmetry the fewer the lines and

[1] National Research Fellow in Chemistry.

[2] Hund, *Linienspektrum*, Julius Springer, Berlin.

[3] Woltjer and Kamerlingh Onnes, Leiden Comm. No. 167C.

[4] Giauque, J. Am. Chem. Soc. **49**, 1870 (1929).

[5] This result might particularly be expected for Gd^{+++} ion for as Kramers has pointed out, S levels as a first approximation do not split in crystalline electric fields. H. Kramers, Proc. Amst. Acad. **32**, 1176 (1929).

[6] Spedding and Nutting, Phys. Rev. **38**, 2294 (1931); J. Am. Chem. Soc., January, 1933.

the less the overall spread of the multiplet.[7] Therefore the excited levels are greatly affected by the crystalline fields and these multiplets arise when the original levels become non-degenerate, because of the fields.

In a letter to *The Physical Review*[8] it was stated that the lines around 2700A in the Gd^{+++} ion in solids do not split into two components, as had been reported previously,[9] but that they split into several (usually nine), and that the apparent doublets were due to intense outer components which were unresolved. Since then these lines have been investigated in more detail, as well as lines at 3100A and 3050A, and this paper will give the experimental data observed.

Monoclinic crystals of $GdCl_3 \cdot 6H_2O$ were chosen to be studied first, as its spectrum had been studied in some detail and many of the lines of its multiplets were well separated from one another so that their Zeeman patterns would not overlap. Also the Paschen-Bach effect would be small.[10]

Experimental Procedure

A large single crystal of $GdCl_3 \cdot 6H_2O$ which crystallizes in flat plates with its flat faces perpendicular to the *b* or symmetry axis was mounted on the end of a long rod. The whole was placed in a large glass Dewar that had a small square quartz Dewar sealed to its bottom by means of quartz glass seals. The quartz Dewar fitted in between the poles of a large electromagnet which were about 1.5 cm apart. The crystal was thus immersed in a cooling liquid and could be raised, lowered, or rotated as desired.

Most of the photographs were made with the light parallel to the *b* axis and the field parallel to the *a* or *c* axis. In one case the crystal was rotated about 15° about the *a* axis. (Figs. 2, 3, 4.)

The source of light was a H_2 discharge of the Bay and Steiner type. A Hilger (185) Littrow type 3 meter spectrograph was used for the earlier work. This later was supplemented by the prism from a smaller Hilger instrument so that the spectrograph was effectively a three prism instrument with a dispersion of about 1.4A per mm at 2700A.

In the study of the lines at 3100A two additional prisms, were added, giving effectively a seven prism instrument with a dispersion of about 9A per mm at 3000A. These prisms were very generously lent us by the Physics Department while their spectrograph was being rebuilt. While the resolving power of the instrument did not increase in proportion nevertheless it was possible to resolve lines which were not resolved before.

The tremendous dispersion and loss of light in the optical path made very long exposures necessary. Thus the exposures varied from 30 to 100 hours, depending on the size of the crystal and the region of the spectrum investigated. Only a few plates at this dispersion were made in the 2700A region as the general absorption in the crystal made necessary exposures of excessive length.

While increased temperature tends to broaden the lines, it was found that the components could be resolved at liquid nitrogen temperatures and as liquid hydrogen runs of such long duration were impracticable most of the photographs were taken at 78°A.

The room containing the spectrograph was of course thermostated to 0.1°C.

Results. Zero Fields

The positions of the absorption lines from various crystals are in general quite reproducible; however, this is no longer the case if the crystals are strained as is frequently the case when they are grown rapidly in contact with some object such as the side of the beaker. Then some lines are broadened, others seem to be resolved into two or three components and still others are not noticeably affected. (See Fig. 1 spectra made with Hilger 185, 3 prisms instrument.) The broadening is particularly noticeable if the light travels parallel to the flat faces where its path length along the strained region is long.

[7] Bethe, Ann. d. Physik **3**, 133 (1929), has predicted such behavior from theoretical grounds.

[8] Spedding, Phys. Rev. **38**, 2080 (1931).

[9] Freed and Spedding, Phys. Rev. **38**, 670 (1931).

[10] As pointed out, crystals of higher symmetry have their lines very close together so that at fields where the components can be resolved the patterns will overlap and strong Paschen-Back effects will be present. However, we hope to be able to study a hexagonal crystal in the near future.

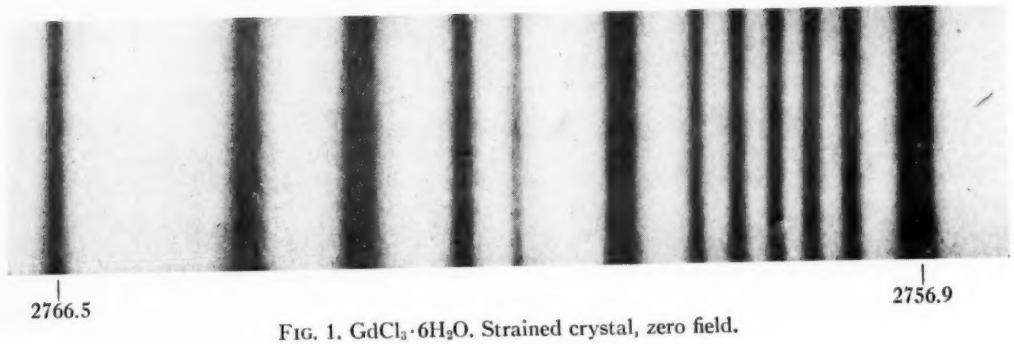


FIG. 1. $GdCl_3 \cdot 6H_2O$. Strained crystal, zero field.

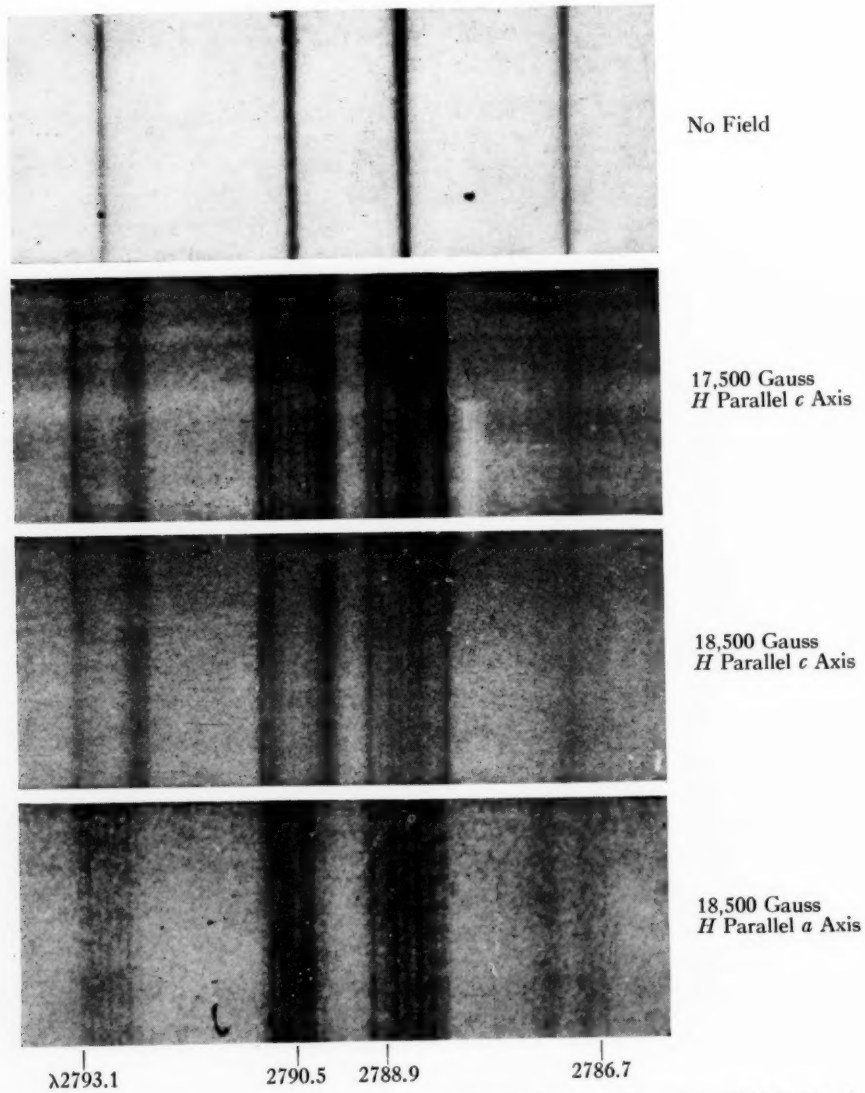


FIG. 2. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel *b* axis, temperature, 78°A.

Repeated cooling tends to strain the crystals and they tend to break up into fragments. For these reasons crystals can be used for only one or two runs.

Just as is to be expected no difference in the position of the lines could be detected when the light traversed the crystal in different directions. The intensities and polarizations of the lines, however, were quite different.

Effect of Magnetic Fields

For a description of the effect of magnetic fields on the lines it was thought best to reproduce microphotometer curves of typical lines and multiplets. (See Figs. 2–8.) While the large grain of the Speedway plates tends to show up under the high magnification used and to mask the lines so that components which are visible to the eye do not show nevertheless enough components do show to give a very good idea of the patterns. Across the face of each print a scale has been drawn the divisions of which are 2ω where ω equals the normal Larmor splitting for that field strength.

The reproductions and curves are self-explanatory so in order to conserve space the reader can obtain the details from the curves and, attention will be called only to a few striking points.

Lines 2786 to 2793A

All lines split into nine components with a separation of approximately 2ω between them. The intensities of the component vary greatly depending on the direction of the field. In some cases the outer components are the more intense, in others, the inner. The separations are not exactly equal, the components toward higher frequencies being usually a little closer together than those towards the red. This inequality becomes much greater at fields where the Paschen-Back effect is definitely present. The intensities of the lines are also not symmetrical about the center.

For some lines in certain directions of the field the components became blurred. However, polarized spectra tended to show these were actually sharp but were blurred because of overlapping of the lines.[11]

Lines at 2766A, 2764A, 2745A and 2743A

These lines behaved very similarly to the above. The rest of the lines in these multiplets were very close together so that their Zeeman components overlapped. They are not reported here, however, where the patterns could be observed, and where the Paschen-Back effect was not pronounced the 2ω separations could be clearly seen. (See Figs. 9 and 10.)

Lines at 3110A, 3112A, 3115A and 3117A

These lines behaved very much like the above except that in the directions photographed fewer components were observed. More components existed, however, as photographs made with lower dispersion in other directions of the field, showed envelopes of the components where these outer ones must have been present.

Also the components of these lines tended to be more diffuse in some directions of the field showing a dependence of the patterns on field direction.

Lines at 3057A, 3061A, 3065A

These lines behaved similarly to those at 3100A. In general the more diffuse the lines the greater the dissymmetries in their intensities and positions. All the lines became diffuse with fields above 20,000 gauss where the Paschen-Back effect becomes pronounced.

There were some indications that the separation of the components did not decrease linearly with the field but this could not be determined with certainty because of the blurring together of the components on account of their width.

Some longitudinal photographs were attempted but because of the long optical path through the pole pieces and the scattering of light at glass faces of the Dewar no spectra were obtained at liquid N_2 temperatures. One photograph was obtained at room temperature where the b axis

[11] While the intensity was too low to use the small nicols we had available, some photographs were obtained where the light was elliptically polarized by passing it through the Cornu prisms used as four 30° instead of two 60° prisms. The two rays were separated by this means by about 15 mm on the plate, the ordinary ray being very intense and the extraordinary ray faint.

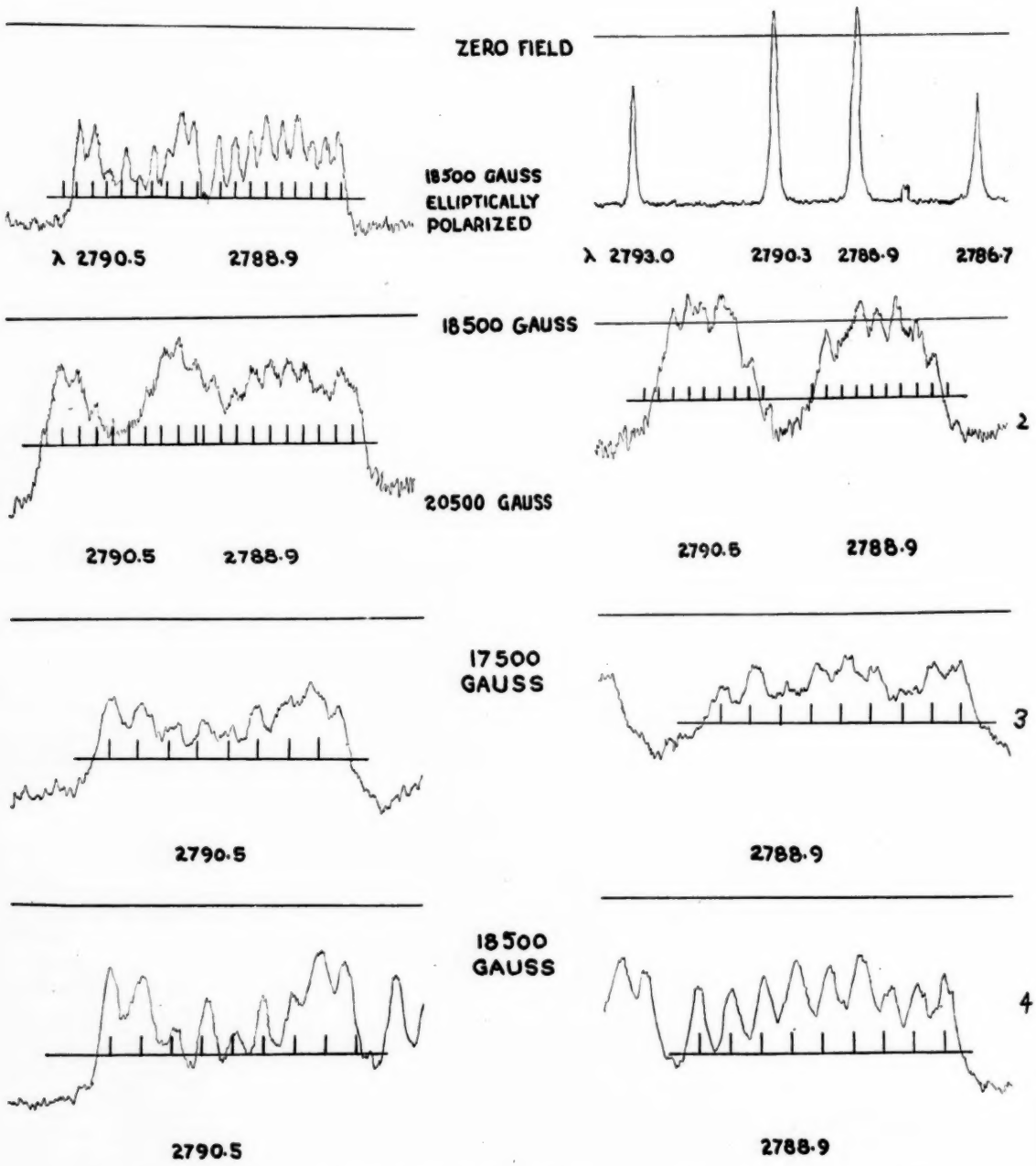


FIG. 3. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel b axis, temperature, 78°A. (Magnification × 23.)

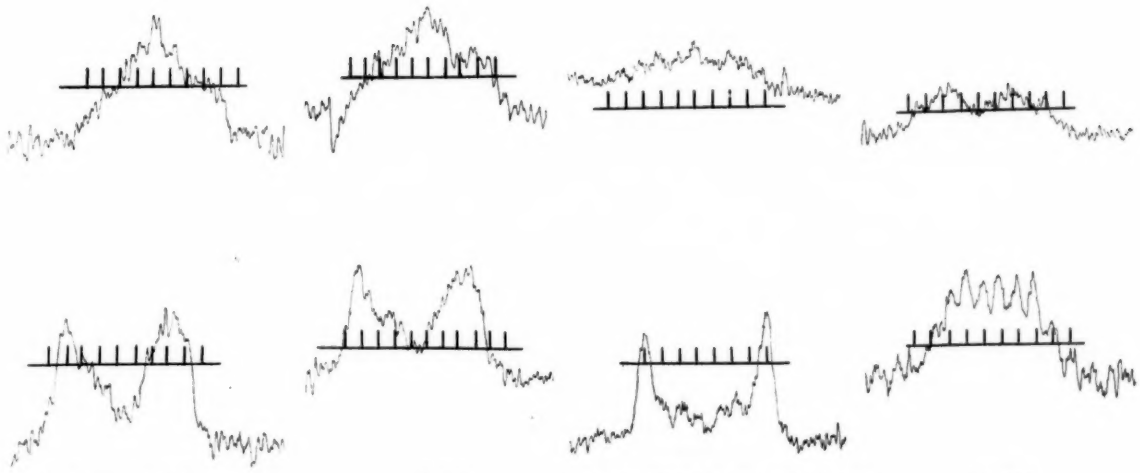


FIG. 4. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel b axis, temperature, 78°A. Upper curves, λ2786.7. Lower curves. λ2793.0. (Magnification × 23.)

was parallel to the field and the envelopes of the components were very similar to those observed in the transverse effect.

DISCUSSION OF RESULTS

While the evidence is not yet complete enough to state with any certainty the nature of the magnetic behavior in solids, many facts have been presented which any theory advanced must take into account.

The theory put forward by the writer in a letter to *The Physical Review*, while not proved, will account for all the observed facts.[12]

It is known from magnetic susceptibilities that the basic level, a $4f^7$, $^8S_{7/2}$, is split into eight components with 2ω separation between them and as the absorption lines are split into components with this separation the excited levels must also be split by this amount.

The fact that the magnetic susceptibilities of the rare earths show that the $4f$ electrons are coupled by Russell-Saunders coupling seems to eliminate terms arising from a $4f^7$ configuration as the three factors of such terms are usually different for each term and are rarely equal to two. Also, when the fields are not strong enough to destroy the R.S. coupling the selection rule for $\Delta n = 0$, $\Delta 1 = 0$ should be effective and the transitions forbidden.

Therefore the excited states must arise from a $4f^6 5x$ configuration and one might expect that the completed $5s$ $5p$ shells which partially shield the $4f$ electrons from the neighboring ions would also partially shield them from the $5x$ electron. The $4f^6$ electrons would then couple together with R.S. coupling to give a resultant such as $^7F_6$, $^7F_5$, etc. The $5x$ electron would be outside the kernel where it would be subjected to the strong electric fields of the neighboring ions.

As the external magnetic field is usually weak with respect to these fields it would not be able to orient the orbit of this electron. While the electron in travelling about the gadolinium ion will have a magnetic moment, because of the strong electric fields present, its direction will be constantly varying so that the total moment of the atom due to this electron will be zero. This moment, however, will be exerted on resultant moment of the inner electrons and as they are free to orient will carry them with it so that their moment will also precess out. The spin of the external electron, however, will not be firmly coupled with the orbital moment as it will resemble very much the circular type orbits of the alkali atoms and it would orient rather freely in a magnetic field. Thus all the excited

[12] This theory also explains the abnormal behavior of the magnetic susceptibility of samarium ion. Spedding, J. Am. Chem. Soc. **54**, 2593 (1932).

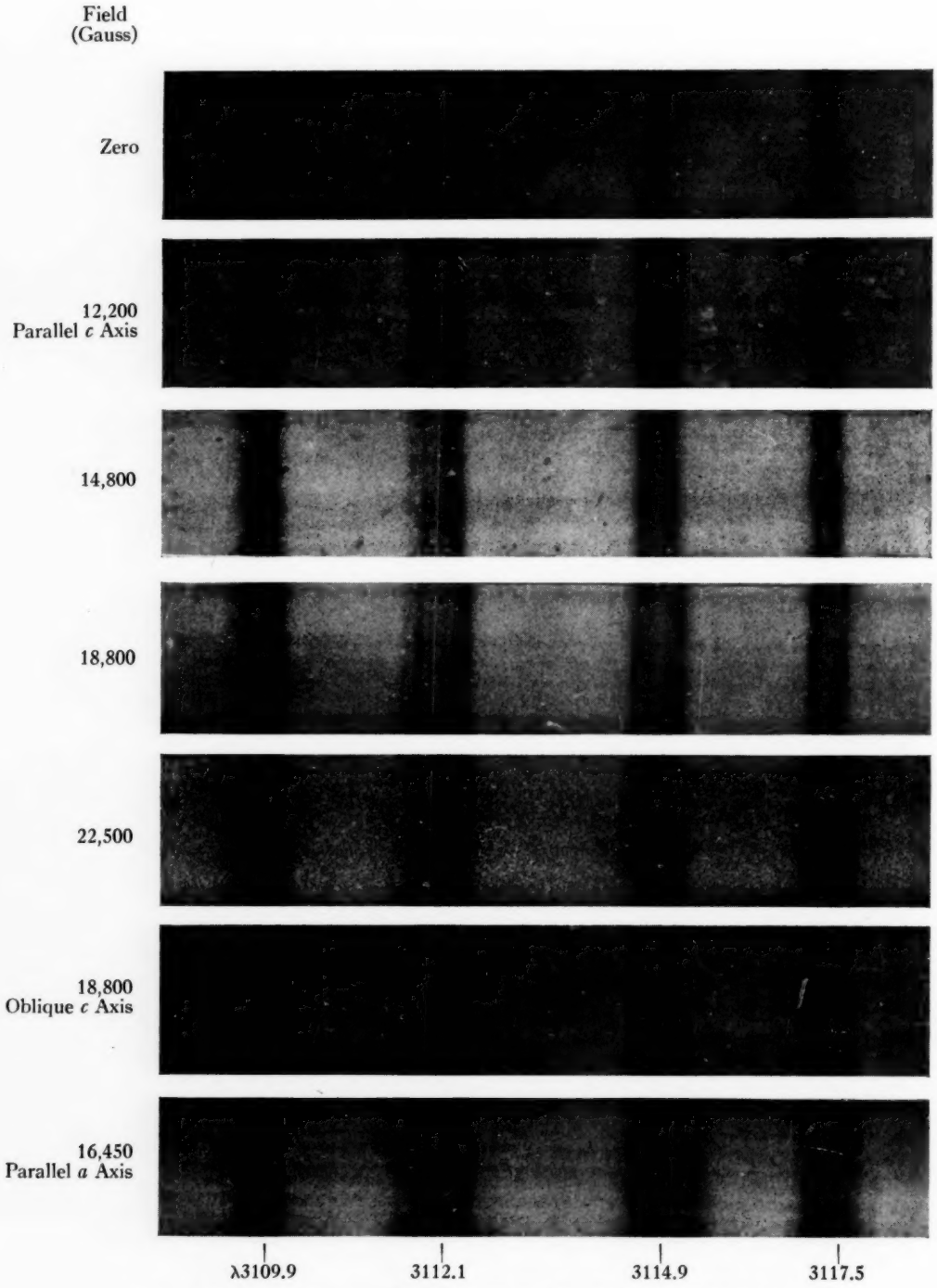


FIG. 5. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light parallel *b* axis.

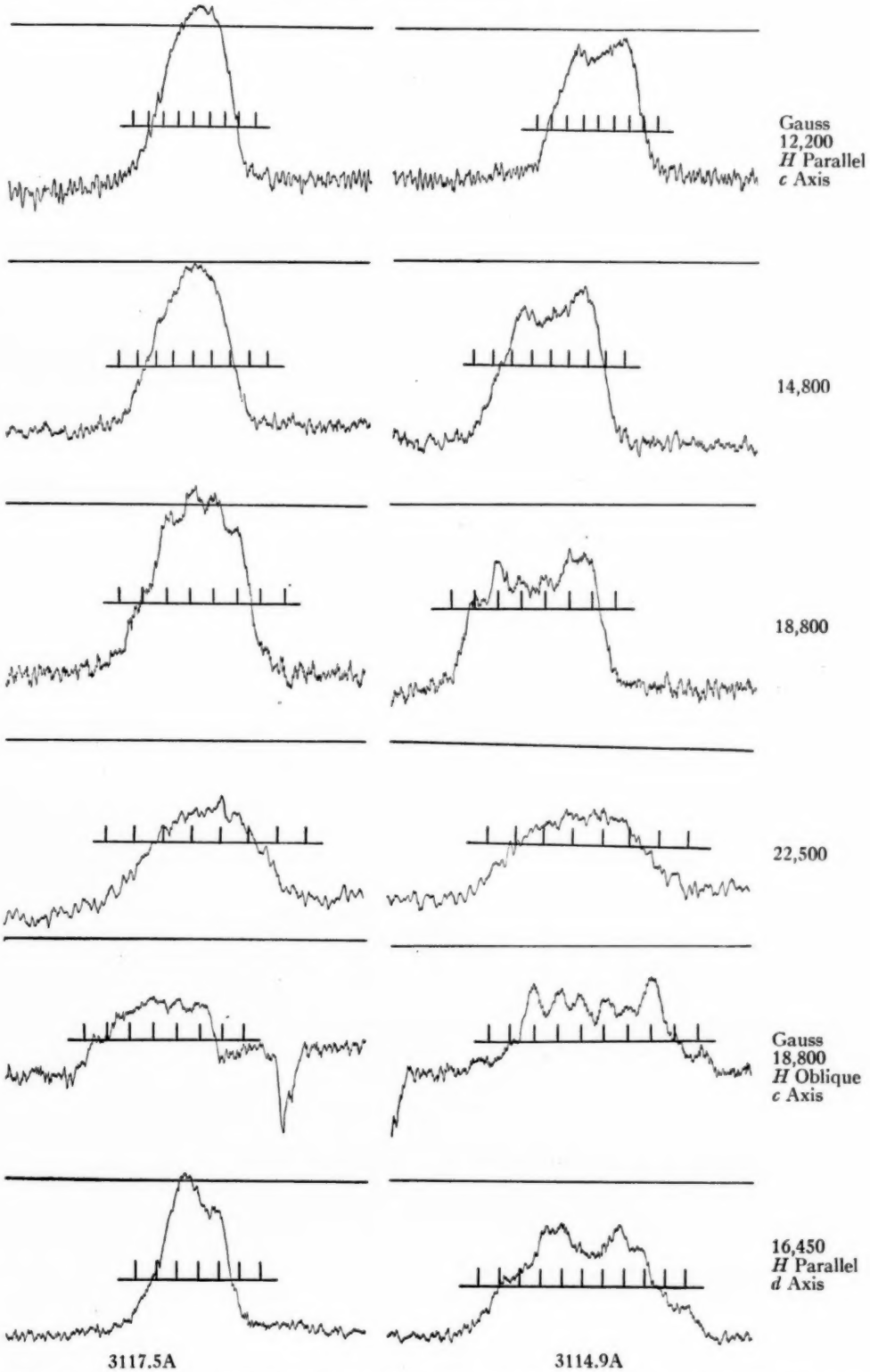


FIG. 6. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel to *b* axis. (Magnification × 21.)

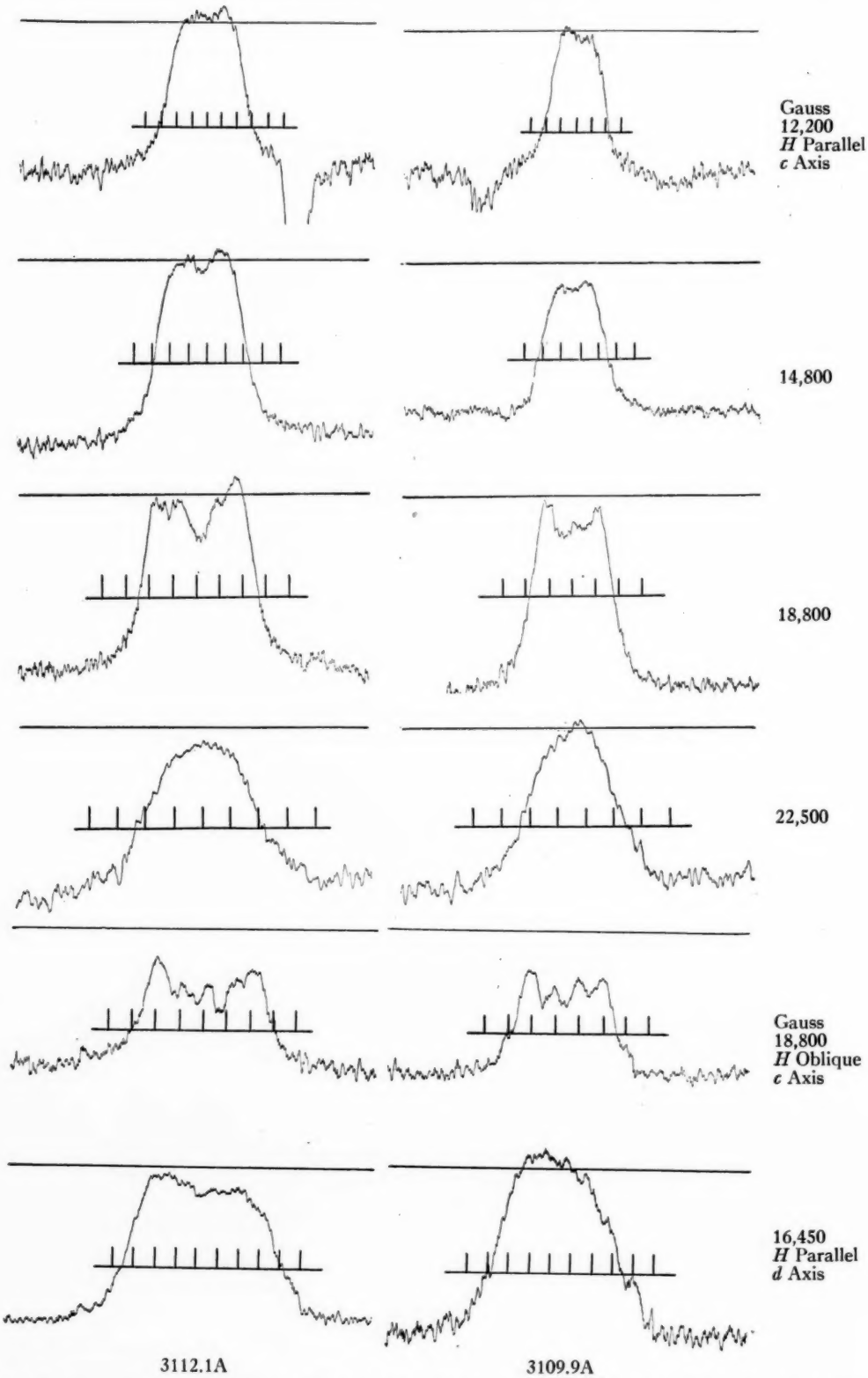


FIG. 7. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel to *b* axis. (Magnification × 21.)

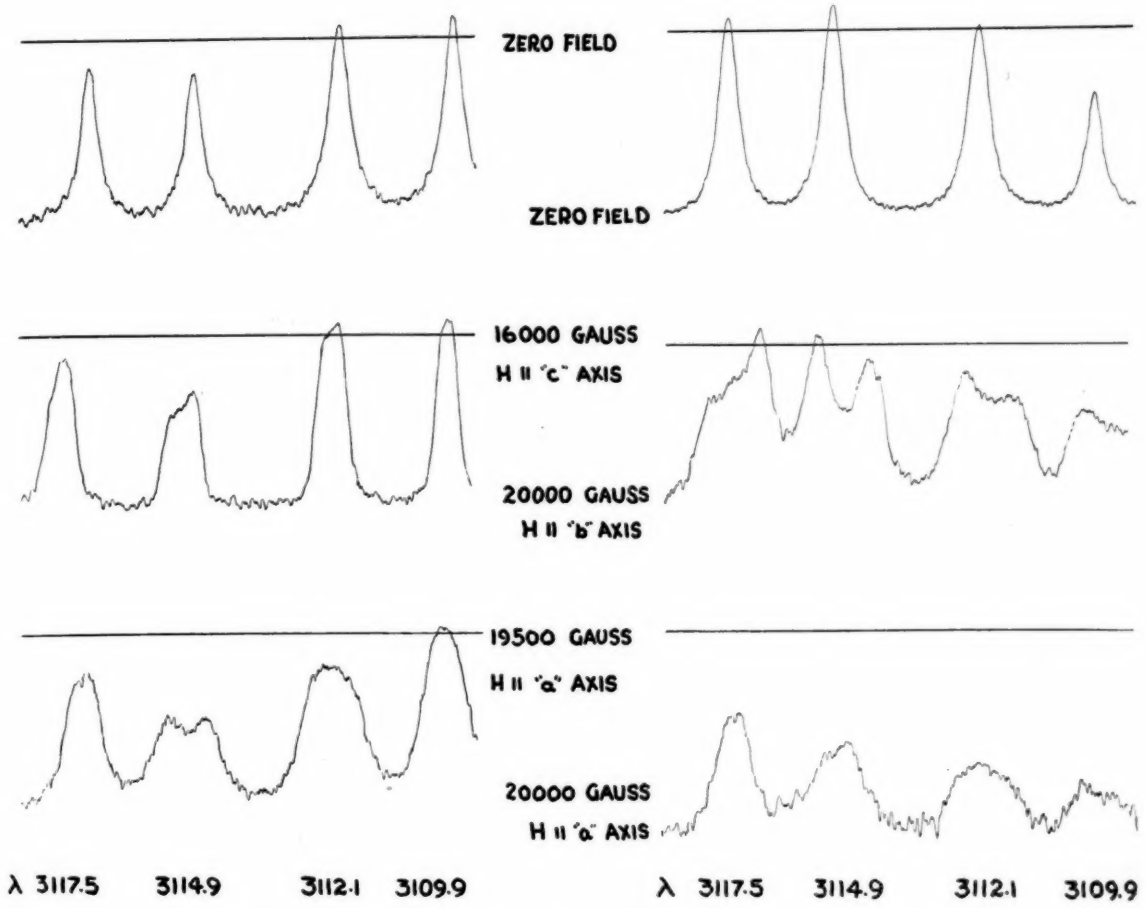


FIG. 8. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Temperature, 298°A. (Magnification × 21.)

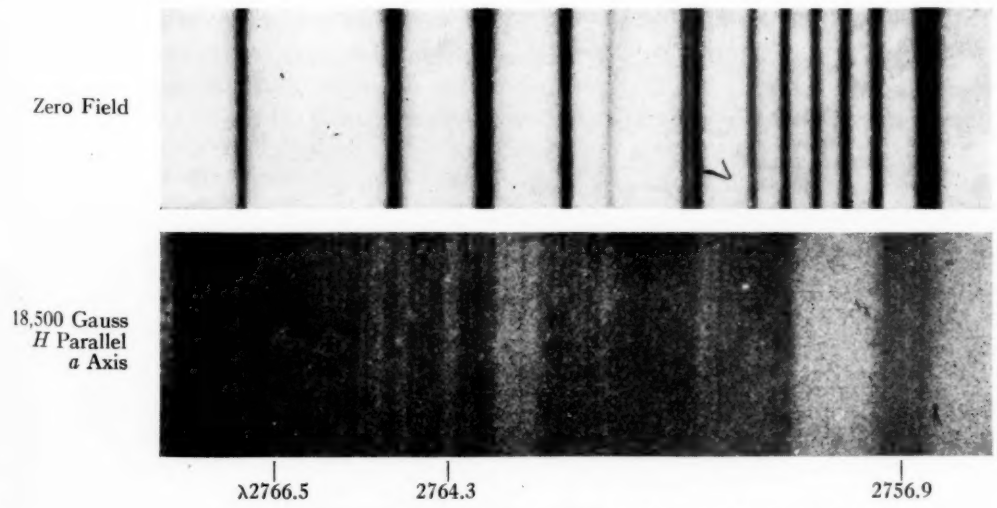


FIG. 9. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. Light ray parallel *b* axis.

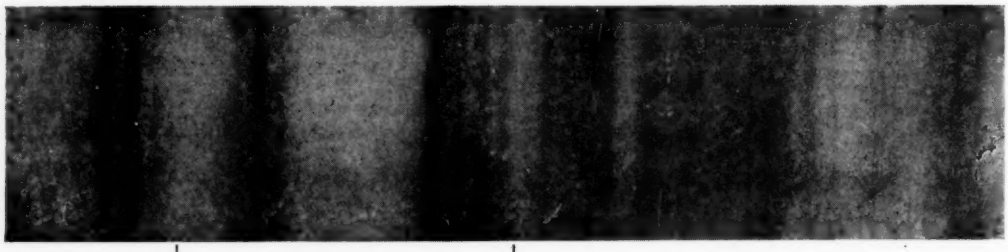


FIG. 10. Transverse Zeeman effect in $GdCl_3 \cdot 6H_2O$. High dispersion 78°A. Light ray parallel b axis. H parallel c axis.

levels regardless of their nature will split into two in a magnetic field with 2ω separation.

Bethe has shown that in the crossed electric and magnetic fields which are present in a crystal the selection rules $\Delta m = \pm 1$ or 0 breaks down. If all transitions are permitted, nine lines will be observed and this is just what is observed in most of the lines investigated. It should be mentioned that this type of coupling represents an ideal case and that the actual coupling will vary from level to level. In the case of Gd^{+++}, however, the actual case seems to be very close to the ideal one. (See Fig. 11.)

In strong fields where the magnetic field splitting becomes of the same order of magnitude as the crystal splitting a Paschen-Back effect will occur and the levels will split unsymmetrically. The observed lines will first blur and then resolve into two components. Also at low fields if the energy of coupling of the spin to the orbit is appreciable, dissymmetries will appear. A third factor which would tend to cause dissymmetries in the splittings is that if the second order terms of the crystal fields caused an appreciable splitting of the basic level the eight components would not be equally spaced in a magnetic field. The photographs seem to show such a condition to be present.

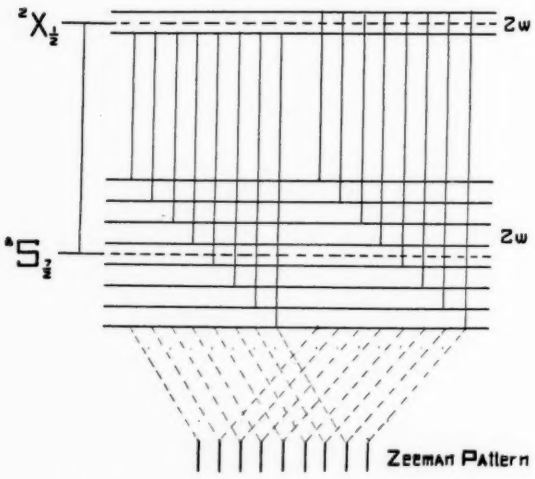


FIG. 11. Theoretical Zeeman effect in solids, Gd^{+++}.

Still another factor which becomes important as soon as the orbital moments begin to contribute to the splitting is that two or more types of gadolinium ions may be present in the crystal lattice. Thus if the unit cell contains more than one gadolinium ion (as it very likely does in $GdCl_3 \cdot 6H_2O$) the dissymmetries of the levels for the different atoms will be different. For even though the atoms are crystallographically identical, they no longer remain so when the external field is applied. The field vector will make different angles with the atoms which are mirror images of each other.[13]

As the lines arising from these levels are superimposed on each other when the dissymmetries occur the lines will blur very badly.

The writer wishes to thank the Chemistry Department for the fine cooperation it has shown him in these researches, and for obtaining the large spectrograph and magnet which made this work possible.

[13] Professor Pabst and the writer are investigating these crystals by x-ray means to determine the size of the unit cells and hope to have results soon.

The Dependence of the Dielectric Constants of Gases on Temperature and Density*

H. H. Uhlig, J. G. Kirkwood and F. G. Keyes, *Massachusetts Institute of Technology*

(Received December 2, 1932)

In two earlier communications, the results of a study of the influence of temperature and pressure on the dielectric constants of carbon dioxide and ammonia have been reported.[1] Since that time the investigation has been continued. The measurements on carbon dioxide and ammonia have been repeated and extended. In addition three new gases, nitrogen, methane and hydrogen have been studied over a wide range of temperature and density. It is the object of the present article to report upon this recent work.

The apparatus employed in the measurements was essentially the same as that used in the earlier work. The manipulation of the gases as well as the measurement and regulation of temperature and pressure were carried out as before. Certain mechanical refinements have been introduced in the construction and calibration of the electrical circuits, which should contribute to greater accuracy. However, since the methods remain the same, only a brief résumé of the general procedure will be given here.

The heterodyne beat method was used throughout the work. Beats were produced between a crystal controlled oscillator operating at a frequency of 1010 kc and a tuned grid oscillator which contained the measuring circuit. After amplification this beat note could be compared with that note of an electrically driven tuning fork. The measuring circuit contained the gas condenser, specially constructed to reduce elastic deformation to a minimum and a precision condenser (General Radio Variable Air Condenser, type 222) calibrated at the Bureau of Standards. In addition there was a comparison condenser, adjusted before each set of measurements to the capacity of the evacuated gas condenser. The two could be alternately inserted in the circuit by means of a low capacity switch. Measurements were taken in the following manner. The gas was introduced at the desired temperature and pressure. By varying the precision condenser the circuit could be brought into near resonance with the crystal controlled oscillator, and the beat note counted. The precision condenser reading was then recorded and the comparison condenser switched into the circuit in place of the gas cell. The precision condenser was again varied until the original beat note was restored and a second reading taken. From these two readings the dielectric constant was calculated.

The condenser circuit was kept as simple as possible to eliminate extraneous capacities. The gas condenser G was connected in parallel with a variable capacity consisting of the precision condenser P in series with a single fixed condenser C. The capacity C determined the sensitivity of the circuit. Fixed mica condensers ranging from $200\mu\mu f$ to $1000\mu\mu f$ were used, depending upon the magnitude of the dielectric constant to be measured. These condensers, the gas condenser and all lead capacities were determined by direct comparison with the precision condenser. A change in capacity ΔG of the gas condenser could be calculated from two readings of the precision condenser by means of the following formula:

$$\Delta G = C^2(P_1 - P_2)/(P_1 + C)(P_2 + C).$$

As a final check on the most troublesome part of the calibration, that of the fixed capacity C, a standard variable condenser was inserted in the circuit in place of G. The capacity of this condenser was varied by an amount comparable to but necessarily larger than the dielectric change to be measured. This change in capacity was first measured with C in the circuit and calculated by means of the above formula. Then C was shunted out and the trial condenser left directly

* Contribution No. 295 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

[1] F. G. Keyes and J. G. Kirkwood, Phys. Rev. **36**, 754, 1570 (1930).

in parallel with the precision condenser. From a second reading the same capacity could be obtained by direct comparison with the precision condenser. By the two methods a capacity of $40\mu\mu f$ could be checked to within one part in a thousand. From the formula it would appear that the relative error produced by an error in C should not differ greatly from this for the much smaller capacity increments produced by the dielectric.

At each temperature a number of sets of successive measurements at regular pressure intervals were made. To each such set certain corrections had to be applied. First there was a small correction for change in the dimensions of the gas condenser due to compression of the walls. It was calculated from the dimensions of the cell and the compressibility of the steel of which it was constructed. This correction seldom exceeded one percent of the value of $\epsilon-1$ (dielectric constant minus one) and was approximately independent of the pressure. A second correction of the same order of magnitude had to be applied for minute extraneous capacity changes attending the introduction of the gas into the condenser. This was calculated for a given set of measurements from the intercept obtained by plotting the function $(\epsilon-1)/(\epsilon+2)$ with density and extrapolating the straight line to zero density.

Of the gases used in the measurements, some were prepared in the laboratory, and others obtained from commercial sources. Carbon dioxide was prepared by heating C.P. sodium bicarbonate. It was carefully dried and finally sublimed several times *in vacuo* before being admitted to the apparatus. Commercial synthetic ammonia was distilled into a small reservoir and allowed to stand over metallic sodium several weeks before being used. Nitrogen and electrolytic hydrogen were obtained from the Air Reduction Sales Company. Their purity was claimed to be better than 99.5 percent. Methane was furnished by the DuPont Company. An analysis showed it to be better than 99.9 percent pure. The three latter gases were all allowed to stand over phosphorus pentoxide before use.

The gas densities which were necessary for the correlation of the data were obtained from the following sources: carbon dioxide, Amagat[2]; ammonia, Beattie and Lawrence[3]; hydrogen, Holborn and Otto[4]; methane, Keyes and Burks[5]; nitrogen (10–100 atm.) Holborn and Otto,[4] (100–250 atm.) Bartlett.[6]

The experimental results are listed in the accompanying tables. They include measurements on carbon dioxide, nitrogen, hydrogen and methane at 0° and 100°C; and on ammonia at 50°, 100°, 150° and 200°C. The new values for carbon dioxide and ammonia are in excellent agreement with the earlier measurements at high densities. At the lower densities, however, the new values are somewhat higher than the old, the maximum deviation being about 2.0 percent.

A relation between the dielectric constant of a substance and structure of its constituent molecules is furnished by the classical theory of dielectrics.[7] This relation is contained in the familiar Clausius-Mosotti law, which states

$$[(\epsilon-1)/(\epsilon+2)]V=(4\pi/3)N\bar{p}, \qquad (1)$$

where ϵ is the dielectric constant, V the molal volume, and N the Avogadro number. The polarizability $\bar{p}$ is the mean electric moment induced in a molecule by an homogeneous field of unit strength. It may be calculated by means of the formula of Debye

$$\bar{p}=\alpha+\mu^2/3kT, \qquad (2)$$

where α is the moment induced by deformation of the electrical structure of the molecule and μ is the permanent dipole moment of the molecule. The validity of this formula is subject to certain conditions, which are probably fulfilled in the present experiments. The Clausius-Mosotti function $(\epsilon-1)V/(\epsilon+2)$ is usually referred to as the molar polarization.

The molar polarization, P_0, has been plotted as a function of density for carbon dioxide, methane, nitrogen and hydrogen in Fig. 1, and for ammonia in Fig. 2. It increases slowly with the density in the case of carbon dioxide and ammonia, but is

[2] Amagat, Ann. de Chimie et de Physique **29**, 68 (1893).

[3] Beattie and Lawrence, J. Am. Chem. Soc. **52**, 6 (1930).

[4] Holborn and Otto, Wiss. Abh. Tech. Reich. **9** (1), 163 (1925).

[5] Keyes and Burks, J. Am. Chem. Soc. **49**, 1403 (1927).

[6] Bartlett, J. Am. Chem. Soc. **52**, 1382 (1930). (W. Deming and L. Schupe.)

[7] See H. A. Lorentz, *Theory of Electrons*, p. 305 (1923); P. Debye, *Polar Molecules*, pp. 1–10 (1929).

TABLE I. *Dielectric constant of carbon dioxide.*[8]

Pressure (atm.)	$\epsilon-1$	Molal volume (cc)	Density mols/liter	$\frac{\epsilon-1}{\epsilon+2}V$
		100°		
20	0.01578	1461	0.68	7.65
30	.02457	947	1.06	7.69
40	.03382	691	1.45	7.70
50	.04366	535	1.87	7.67
60	.05411	434	2.30	7.69
70	.06520	361	2.77	7.68
80	.07752	306	3.27	7.71
90	.09071	263	3.80	7.72
100	.1048	229	4.37	7.73
125	.1452	168.5	5.95	7.78
150	.1913	130.5	7.66	7.82
		0° (liquid)		
50	0.6044	46.75	21.39	7.84
75	.6190	45.56	21.95	7.79
100	.6305	44.97	22.24	7.81
125	.6413	44.34	22.55	7.81
150	.6509	43.78	22.84	7.81
175	.6591	43.31	23.09	7.80
200	.6678	42.85	23.34	7.80

TABLE II. *Dielectric constant of methane.*

Pressure (atm.)	$\epsilon-1$	Molal volume (cc)	Density mols/liter	$\frac{\epsilon-1}{\epsilon+2}V$
		100°		
20	0.01345	1511	0.6618	6.77
40	.02750	746.9	1.339	6.78
60	.04164	493.3	2.027	6.75
80	.05615	367.0	2.725	6.74
100	.07113	291.9	3.426	6.76
125	.09005	232.6	4.299	6.78
150	.1089	193.5	5.168	6.78
175	.1275	166.3	6.013	6.78
		0°		
20	0.01918	1068	0.936	6.79
40	.04044	507.7	1.970	6.75
60	.06439	321.5	3.110	6.76
80	.09082	229.4	4.359	6.74
100	.1198	175.8	5.688	6.75

TABLE III. *Dielectric constant of hydrogen.*

Pressure (atm.)	$\epsilon-1$	Molal volume (cc)	Density mols/liter	$\frac{\epsilon-1}{\epsilon+2}V$
		100°		
30	0.00612	1036.0	0.965	2.11
50	.01005	628.0	1.592	2.10
70	.01375	453.0	2.208	2.07
90	.01772	355.8	2.811	2.09
125	.02421	260.5	3.839	2.09
150	.02880	219.7	4.552	2.09
		0°		
30	0.00837	761.3	1.314	2.12
50	.01379	462.4	2.163	2.12
70	.01910	334.4	2.990	2.12
90	.02430	263.4	3.797	2.12
125	.03326	193.9	5.157	2.13
150	.03958	164.1	6.094	2.14

TABLE IV. *Dielectric constant of nitrogen.*

Pressure (atm.)	$\epsilon-1$	Molal volume (cc)	Density mols/liter	$\frac{\epsilon-1}{\epsilon+2}V$
		100°		
10	0.00446	3068	0.3260	4.55
20	.00883	1538	0.6502	4.51
40	.01770	773.1	1.294	4.54
60	.02662	518.8	1.928	4.56
80	.03528	392.1	2.550	4.56
100	.04389	316.4	3.161	4.56
150	.06448	216.5	4.619	4.56
200	.08353	167.5	5.970	4.54
250	.1006	138.4	7.225	4.49
		0°		
10	0.00609	2231	0.4482	4.52
20	.01220	1112	0.8993	4.50
40	.02468	552.7	1.809	4.51
60	.03732	367.4	2.722	4.51
80	.04999	275.4	3.631	4.51
100	.06262	220.7	4.531	4.51
150	.09343	149.5	6.689	4.52
200	.1217	115.9	8.628	4.52
250	.1473	96.84	10.33	4.53

TABLE V. *Dielectric constant of ammonia.*

Pressure (atm.)	$\epsilon-1$	Molal volume (cc)	Density mols/liter	$\frac{\epsilon-1}{\epsilon+2}V$
		200°		
20	0.05718	1867	0.5356	34.91
30	.08879	1219	0.8203	35.05
40	.1225	895.5	1.117	35.13
50	.1583	700.8	1.427	35.13
60	.1974	570.8	1.752	35.24
70	.2391	477.4	2.095	35.24
80	.2849	407.5	2.454	35.34
90	.3342	352.7	2.835	35.36
100	.3888	309.2	3.234	35.48
		150°		
20	0.07232	1636	0.611	38.51
30	.1141	1055	0.948	38.66
40	.1602	763.0	1.311	38.68
50	.2122	586.8	1.704	38.76
60	.2712	468.7	2.134	38.85
70	.3404	383.1	2.610	39.03
80	.4203	318	3.15	39.08
90	.5162	266	3.76	39.05
100	.6344	223	4.48	38.93
		100°		
20	0.0954	1385	0.722	42.69
25	.1243	1076	0.929	42.80
30	.1559	867.3	1.153	42.85
35	.1905	717.7	1.393	42.85
40	.2296	604.3	1.655	42.96
45	.2738	514.0	1.946	42.99
50	.3251	440.4	2.271	43.06
55	.3862	377.5	2.649	43.05
		50°		
15	0.09719	1539	0.6498	48.29

[8] Measurements were taken at ten atmosphere intervals. However, in order to conserve space, only a part of them are given in Tables I–V.

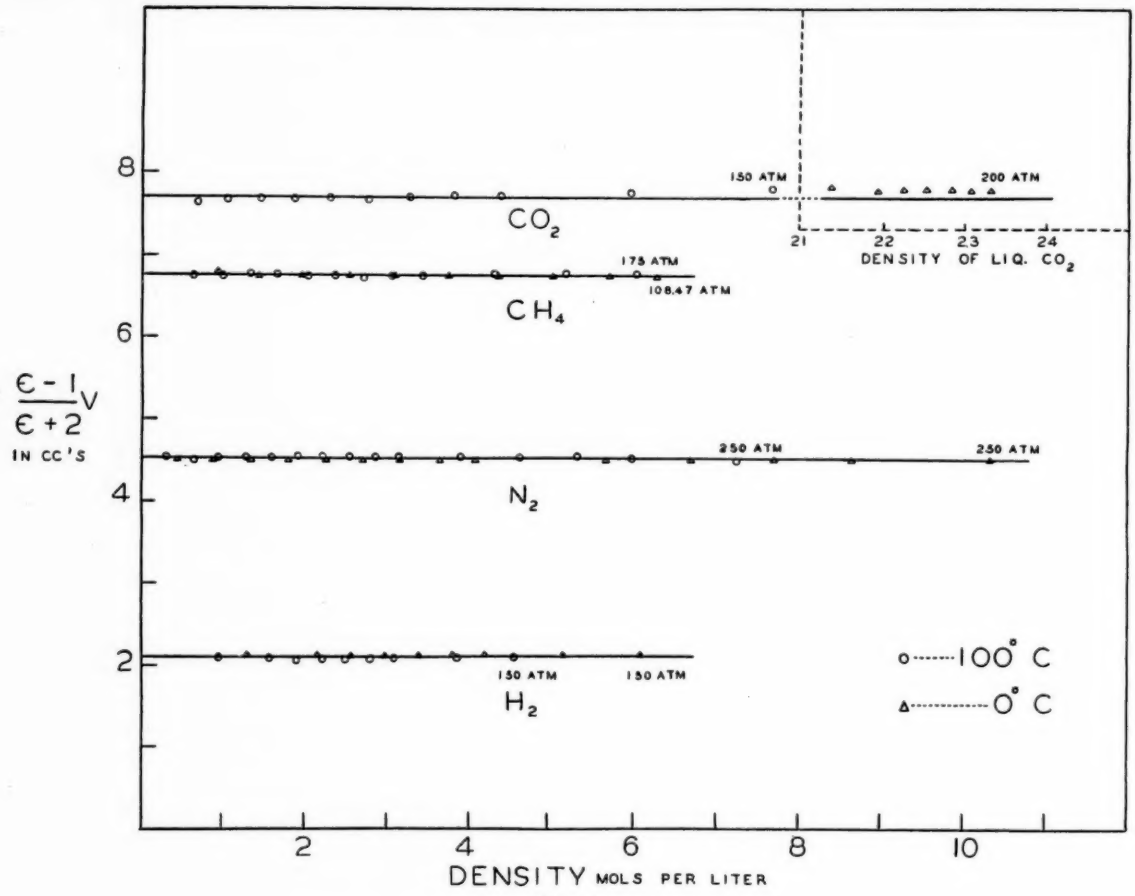


FIG. 1

entirely independent of the density for methane, nitrogen and hydrogen. The molar polarizations of carbon dioxide, methane, nitrogen and hydrogen are independent of the temperature, indicating that the molecules of these substances possess no permanent dipoles. In the case of ammonia, P_0 varies strongly with the temperature. When extrapolated to zero density and plotted as a function of $1/T$, P_0 yields a straight line as predicted by Debye's equation. From the slope of this line the dipole moment of ammonia is calculated to be 1.48×10^{-18} e.s.u. When the product P_0T is plotted as a function of temperature, another line is obtained, the slope of which gives the part of the polarization due to optical and to nonrotational infrared terms. This part P_0^1 amounts to 6.2 cc/mol.

The molar polarizations calculated from the present measurements and extrapolated to zero density agree fairly well with those calculated from low density dielectric constant measurements of other investigators, although they tend

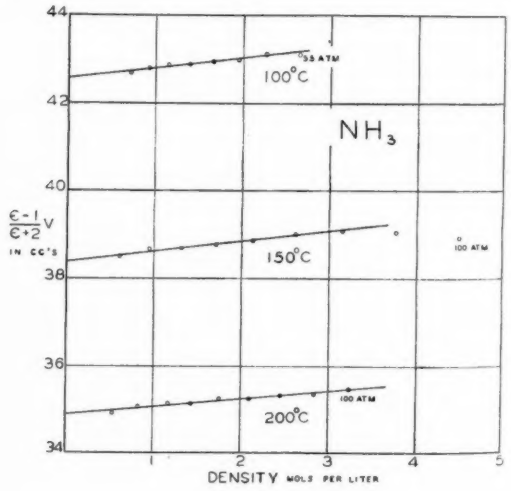


FIG. 2

to be slightly higher. Further, except in the case of ammonia, methane and carbon dioxide, where infrared dispersion terms are known to exist, the molar polarization is in good agreement with the molar refraction extrapolated to infinite wavelength.

Causes for the variation of the molal polarizations of carbon dioxide and ammonia with density have been discussed in the earlier work on these gases. So far no fully satisfactory quantitative explanation has been reached. It is hoped that work now in progress on mixtures of ammonia and nonpolar gases may throw some light on this question.

The Dielectric Constant of Liquid Sulphur*

HOWARD J. CURTIS, *Sloane Physics Laboratory, Yale University*

(Received December 5, 1932)

The dielectric constant and power factor of liquid sulphur were measured by a bridge method at four different audio-frequencies and over the temperature range 118°C to 350°C. The dielectric constant was found to be independent of frequency and equal to 3.520 ± 0.010 at 118°C. A study of the polarization curve shows that liquid sulphur is non-polar. A method was developed for differentiating between that part of the power factor which is due to conductivity and that which is due to molecular friction. The former was found to be large at high temperatures and the latter small at all temperatures. The infrared spectrum of liquid sulphur contains definite absorption bands, which fact shows that its molecules are polar. It is difficult to understand this contradiction, since both measurements seem to give conclusive results.

INTRODUCTION

ACCORDING to Debeye's theory, it should be possible to measure the electric moment of a substance according to the formula

$$\frac{\epsilon-1}{\epsilon+2}\frac{1}{d}=\frac{4\pi}{3}\frac{N}{M}\left(\alpha+\frac{\mu^2}{3kT}\right)=P,$$

where ϵ is the dielectric constant, d the density, N Avogadro's constant, α the molecular polarizability, μ the electric moment, k Boltzmann's constant, T the absolute temperature, and P the specific polarization. This formula has been found to apply quantitatively to gases and non-associated liquids, and qualitatively to associated liquids.

Debye[1] has further shown that if a liquid is quite viscous, the molecules may find difficulty in orienting themselves in the direction of the field. If such a liquid were placed in an alternating field and the frequency increased, a frequency would finally be reached where the molecules could no longer follow the alternations of the field, so that at this frequency the liquid would virtually become nonpolar. Debye calls this a region of anomalous dispersion, and predicts, among other things, that the power factor of the substance should increase markedly in this region. Mizushima,[2] Kitchen and Müller,[3] Smyth[4] and others have obtained qualitative verifications of this theory.

It was thought that a study of an elementary substance might prove to be valuable in clearing up some of the difficulties which still remain; and it was for this reason that sulphur was chosen for the present study.

At the melting point, liquid sulphur is quite mobile. On heating, the viscosity remains approximately constant until about 160°C is reached, when it becomes very viscous, and reaches a maximum viscosity about 180°C, after which the viscosity decreases rapidly at first and then quite gradually up to the boiling point at 445°C. It is one of the few liquids which have a viscosity cycle. Molecular association is known to occur. According to Kellas[5] the sulphur molecule contains eight atoms at the melting point. At 160°C the reaction $3S_8 \rightleftarrows (S_8)_3$ takes place, and goes more strongly to the right as the temperature is increased, and reverses just before it reaches the boiling point.

Taylor and Rideal,[6] from measurements on the heat of dissociation, the heat of vaporization, and the infrared absorption spectrum, conclude

* Part of a dissertation presented for the degree of Doctor of Philosophy in Yale University.

[1] P. Debye, *Polar Molecules*, The Chemical Catalog Company (1929).

[2] Mizushima, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **5**, (79) 201 (1927); **9**, (166) 209 (1928).

[3] Kitchen and Müller, Trans. Am. Inst. Elect. Eng. **48**, (2) 495 (1928).

[4] Smyth, *Dielectric Constant and Molecular Structure*, The Chemical Catalog Company (1931).

[5] Kellas, J. Am. Chem. Soc. **113**, 903 (1918).

[6] Taylor and Rideal, Proc. Roy. Soc. **A115**, 589 (1927).

that the S_2 molecule is definitely polar. However, Rosenthal[7] has measured the dielectric constant of liquid sulphur over a limited temperature range and at a very high frequency, and finds it to be nonpolar. Since the liquid becomes so viscous at high temperatures, one might expect that it would exhibit anomalous dispersion at low frequencies if it were polar. Therefore Rosenthal's result would not seem to be very conclusive. It was thought to be advisable to make the measurements at several low frequencies, and over a wide temperature range.

Apparatus

A diagram of the measuring apparatus is shown in Fig. 1. Part A represents a Hartley oscillator

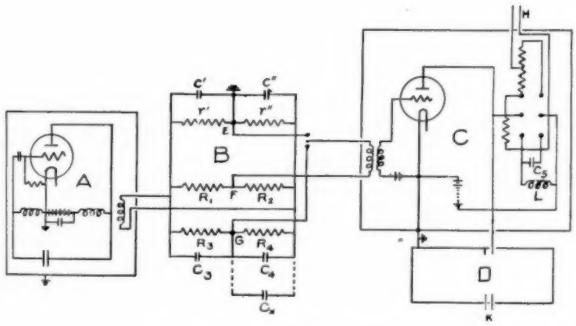


Fig. 1. Diagram of apparatus.

capable of giving a large number of frequencies between 200 and 4000 cycles, placed in a grounded metal box. Part B represents a capacitance bridge of the parallel resistance type. The upper arms consist of resistances R_1 and R_2, which are matched coils of 4000 ohms each. The lower arms consist of condensers C_3 and C_4 shunted by resistances R_3 and R_4. C_3 is a variable air condenser, C_4 is a standard variable air condenser recently accurately calibrated at the Bureau of Standards, and R_3 and R_4 are 100,000 ohm resistance boxes. r', r'', c', and c'' make up a Wagner ground. C_x is the measuring cell, arranged so that it may be placed in parallel with C_4. Every resistance and condenser in the bridge is in a separate grounded metal case, and the arrangement symmetrically placed to diminish the interaction between the various parts.

[7] Rosenthal, Acad. Pol. Sci. et Let. Bull. **8a**, 377 (1928).

Current from the bridge is fed through a transformer to an amplifier C. In the plate circuit of this tube is a combination frequency bridge and wave filter. C_5 is a mica capacitance box, and L is a Brooks inductometer used as a self-inductance. When the double pole-double throw switch is thrown up, the arrangement is a frequency bridge of the usual type and may be balanced for a particular frequency by placing phones at the point H. When the switch is thrown down, the condenser and inductance are put in parallel across the output of the amplifier and act as a wave filter which allows only that frequency to pass. The frequency bridge was calibrated to an accuracy of about 1 percent by means of a General Radio Company calibrated low-frequency oscillator. This arrangement made it a simple matter to measure the frequency and set the wave filter.

The output of this amplifier is fed into another amplifier, which is a 3-stage resistance-coupled amplifier of the usual type. Both amplifiers are placed in separate grounded metal boxes, and high-frequency low pass filters put in the input leads of both. These precautions eliminate external disturbances.

The measuring cell consists of three concentric aluminum cylinders approximately 10 cm in diameter. The outer and inner cylinders are rigidly screwed to an aluminum base, and together make up one plate of the condenser. The middle cylinder, which is shorter than the other two, is separated from them by quartz spacers, and comprises the other plate. The liquid is placed between the outer and inner cylinders and thus completely surrounds the middle one. This eliminates end effects. The effect due to the lead to the middle electrode was found to be negligible. This lead is surrounded by a quartz tube which acts as a spacer and extends outside of the condenser. Thus any leak across the surface of the liquid is eliminated. The spacers were very accurately ground, so that the condenser may be taken apart and reassembled without affecting its capacitance.

The spacers used in the condenser are quartz. Upon investigation it was found that they have an appreciable power factor above 350°C. Moulded magnesium oxide spacers were found to be far superior even at quite low temperatures,

but since sulphur was found to have a very high conductivity above 300°C, the error introduced by the quartz spacers is negligible, and they are used in preference to magnesium oxide on account of their superior mechanical properties.

The measuring cell is placed in a resistance furnace which is run from storage batteries and may be maintained at any desired temperature to within one degree throughout the cell. A thermocouple for measuring the temperature is placed in the liquid sulphur.

Method of Measurement

The dielectric constant of sulphur is determined by measuring the capacitance of the measuring cell with air as the dielectric and again with sulphur as the dielectric. The ratio of these two capacitances gives the dielectric constant.

A strict substitution method is employed in making the measurements so that all lead capacitances and so forth are eliminated. The resistance boxes R_3 and R_4 were found to have so low an inductance that they introduced an inappreciable error. An individual reading of the capacitance is correct to 0.1 percent. In the measurement of the dielectric constant, the effect of the quartz spacers in the measuring cell had to be taken into consideration. There are six spacers at the top and six at the bottom, but three at each end are sufficient to hold the electrodes rigidly in place. The procedure is to measure the capacitance of the air condenser with all 12 spacers in place at a number of temperatures; then remove three at each end and repeat the process. The difference in capacitance at any temperature gives the effect of half the spacers, and by interpolation the true capacitance of the condenser can be found.

It is known that a number of the properties of liquid sulphur depend on its past history. Thus, in order to get consistent results, it was thought advisable to start each run with c.p. crystals of sulphur, melt them very carefully at a temperature just above the melting point; and increase the temperature at about the same rate on all runs. However, it was found that if the sulphur was allowed to stand at a fixed temperature for from two to five hours, depending on the viscosity, the dielectric constant and power factor are independent of its past history. The latter procedure was finally adopted, each run taking about two weeks to complete.

The measurement of the power factor presented some difficulty. A leaky condenser is conventionally represented either as a resistance in parallel or in series with a perfect condenser. When the power factor is small, it makes very little difference which representation is used; but when it is large, it makes a very appreciable difference. Errors in the measured capacitance of greater than 100 percent may be made in this way. It is then necessary to represent the condenser as a combination of resistances in series and parallel with a perfect condenser. Two different types of power losses in condensers with liquid dielectrics are well recognized; the first being due to an ionic conductivity, and the second to molecular friction. It seems reasonable to assume that the former can best be represented by a parallel resistance, and the latter by a series resistance. In his theory Debye completely ignores the conductivity due to ions, and considers the power factor as due entirely to molecular friction. If ionic conductivity is large, it may completely mask the effect due to molecular friction. It was found to be necessary to devise a method of measurement which would separate these two power factors, and at the same time allow a measurement of the true dielectric constant if power factor measurements were to be compared with those predicted by Debye's theory, since the ionic conductivity of sulphur at high temperatures is quite large. For this reason, corrections to the measured capacitance are much smaller in a parallel resistance bridge method than in a series method.

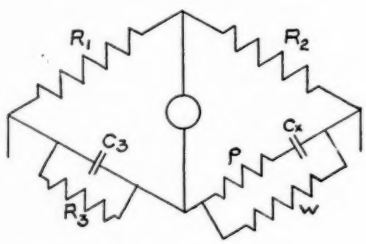


Fig. 2. Equivalent bridge diagram.

Fig. 2 shows the equivalent bridge, where ρ is the fictitious resistance due to molecular friction,

and w that due to ionic conductivity. The bridge shown assumes a nonsubstitution method, but the transition to a substitution method is readily made. The conditions for balance are:

$$\frac{1}{w}\left[\frac{1+\omega^2\rho(\rho+w)C_x^2}{1+\omega^2\rho^2C_x^2}\right]=\frac{1}{R_3}, \quad (1)$$

$$\frac{C_x}{1+\omega^2\rho^2C_x^2}=C_3, \quad (2)$$

where ω is 2π times the frequency, and $R_1=R_2$.

From these it is found that

$$\rho=1/\omega C_x[(C_x-C_3)/C_3]^{1/2} \quad (3)$$

and

$$1/w=1/R_3-\omega[C_3(C_x-C_3)]^{1/2}. \quad (4)$$

Since there are three unknowns, certain assumptions will have to be made. Assume first that the ionic conductivity is not a function of the frequency; that is, that w is constant. Next assume that the frictional resistance varies inversely as the frequency; that is $\rho=\alpha/\omega$, where α is a constant.

These assumptions are justified by their application to sulphur and by the measurements of Bryan[8] who plotted the power factors of a number of liquids against the frequency and found their component parts to vary in this way. Next assume that

$$\rho=(1/\omega C_3)[(C_x-C_3)/C_3]^{1/2}.$$

This amounts to expanding C_x in a power series and dropping the fourth and higher order term in C_3, since C_3 is very small. This assumption greatly facilitates the solution of the equations.

Writing the Eqs. (3) and (4) for two different frequencies, and solving for α and C_x we get

$$\alpha=(1/R_3-1/R'_3)/(\omega C_3^2-\omega' C'^2_3) \quad (5)$$

and

$$C_x=C_3(1+\alpha^2C_3^2+4\alpha^4C_3^4+\cdots). \quad (6)$$

where primes indicate quantities having to do with the second frequency.

Also, $\tan\ \phi_1=\omega\rho C_x=\alpha C_x$; $\tan\ \phi_2=1/\omega R_3C_x$,

where ϕ_1 is the phase angle due to molecular friction, and ϕ_2 is the total phase angle, since $R_1=R_2$. These are the angles between the impedance vector and the resistance vector. To obtain the power factor, which is the cosine of this angle, one merely employs a table of natural trigonometric functions.

Values of α, obtained by computations on different pairs of frequencies, show that it is not strictly a constant. The procedure which was adopted is to call the value of α obtained from two different frequencies the correct value for a frequency which is the mean of the two measured frequencies. By plotting the values obtained from several pairs of frequencies on an α-frequency graph, values of α at any frequency may be obtained. It was found that measurements at four different frequencies are sufficient to determine α over the frequency range used.

Values of the dielectric constant and power factor which were obtained from the first few runs did not agree at all above about 300°C. After a careful investigation it was found that the effect of slight impurities and the past history of the sulphur had nothing to do with this disagreement, as was at first supposed, but the trouble was due to a peculiar polarization phenomenon at the electrodes. It occurred at different temperatures on different runs, and resulted in a greatly increased dielectric constant and frictional power factor in a fairly narrow temperature range. It was found that when a very thick coating of oxide had formed on the aluminum electrodes, successive runs agreed to within the experimental error. To make sure that these were the true values, another aluminum condenser was built having a capacitance about two-thirds that of the original one. After the electrodes had been well oxidized, measurements with this condenser agreed exactly with those of the original one. If any electrode effect had been present, the apparent dielectric constant would certainly have varied with the electrode distance.

Results

The results for a frequency of 312 cycles from one of the first runs is shown in Fig. 3. Curve 1 represents the dielectric constant, curve 2 the frictional power factor, and curve 3 the total power factor. The reason for the concern about the values in the neighborhood of 300°C is quite obvious, as it appears to be a region of anomalous dispersion.

[8] Bryan, Phys. Rev. 22, 399 (1923).

Curves from one of the later runs are shown in Fig. 4. The curves shown are for a frequency of 312 cycles; curves for different frequencies

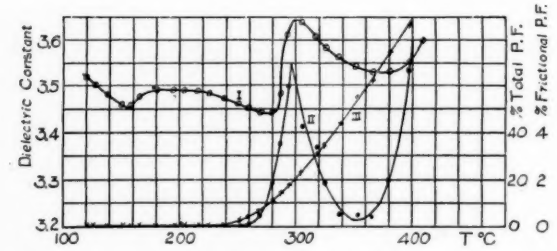


FIG. 3. Results of a preliminary run. I, dielectric constant; II, frictional P.F.; III, total P.F.

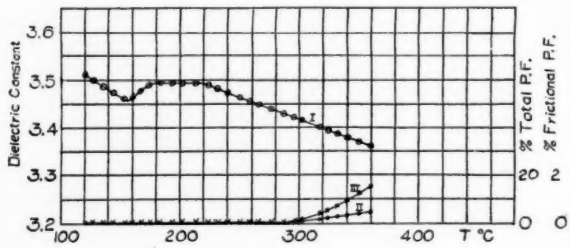


FIG. 4. Results of a final run. I, dielectric constant; II, frictional P.F.; III, total P.F.

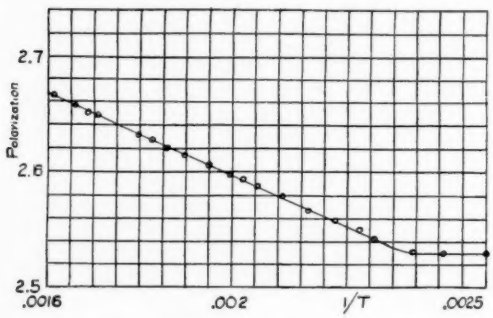


FIG. 5. Polarization curve.

being identical to within the experimental error. Curve 1 gives the dielectric constant, curve 2 the frictional power factor, and curve 3 the total power factor. It will be seen that the apparent anomalous dispersion has now entirely disappeared. The density of sulphur at different temperatures was taken from an article by Kellas[5] which appeared to be the best available. From this the polarization could be computed. This was plotted against the reciprocal of the absolute temperature in Fig. 5, the data being taken from Fig. 4.

Table I shows a typical set of results for a temperature of 231°C. The table is self-explanatory, and values given there may be checked by using the formulas given above.

The error in the measured capacitance of the unknown condenser in each case is estimated at less than 0.1 percent. Values of the dielectric constant obtained on different runs check to within 0.3 percent, and this was taken as the experimental error. The estimated error in the total power factor is 1 percent, and that in the frictional power factor is 5 percent.

It will be seen from the polarization curve that for temperatures from 118°C to 158°C the polarization is independent of the temperature and has a value of 0.2528 ± 0.0008 cc/g. In the region 148°C to 120°C, Rosenthal[7] gives the value 0.2628 by direct measurement at high frequency, and the value 0.318 by measurements on dilute solutions of sulphur in carbon disulphide.

It will also be noted from the polarization curve that above 158°C the polarization decreases directly as $1/T$, instead of increasing as it would if it were a polar substance. This, together with the fact that the frictional power factor is always quite small, shows that liquid sulphur is definitely nonpolar.

It is interesting to compare these results with the results of Taylor and Rideal[6] on the infrared absorption spectrum of sulphur in various forms. They found the same definite absorption bands

TABLE I.

Temp.	Freq.	Meas. cap. $\mu\mu F$	$\frac{1}{R_3}\times 10^{10}$	$\alpha\times 10^{-5}$	Corr. cap. $\mu\mu F$	Diel. const.	% Fr. P.F.	% Total P.F.	Dens.	P cc/g
231	312	2173.9	170	6.4	2169.8	3.486	0.14	0.40	1.7390	0.2605
231	548	2172.4	215	6.9	2168.3	3.485	0.15	0.27	1.7390	0.2604
231	1248	2169.9	372	6.5	2165.8	3.482	0.14	0.22	1.7390	0.2602
231	2829	2168.2	531	2.8	2164.1	3.480	0.06	0.14	1.7390	0.2601

appearing in all forms. Shaefer and Matossi,[9] in discussing these results, assume that S_2 is the fundamental entity in all forms of sulphur, that it has a large electric moment, and always remains free to rotate. Thus these results seem to directly contradict the results given above. Similar contradictions have previously been noted and are very interesting, although no plausible explanation of them can be offered at the present time.

[9] Shaefer and Matossi, *Das Ultrarote Spektrum*, Julius Springer (1930).

The Thermal Decomposition of Ethylene Iodide

L. B. ARNOLD, JR. AND G. B. KISTIAKOWSKY, *Chemical Laboratory, Harvard University*

(Received December 3, 1932)

The homogeneous gaseous decomposition of ethylene iodide has been studied in the temperature interval 205°–230°C. It is found that two simultaneous reactions occur to give the same final products, ethylene and iodine. One is a reaction catalyzed by iodine atoms, similar to that found to occur in solutions. The other is a unimolecular decomposition. The activation energies of the two reactions are 31,400 cal. and 37,500 cal., respectively. It is shown that the results for the iodine catalyzed reaction in solution and in the gas phase are in agreement indicating that the solvent has only a slight effect, if any, on the reaction rate.

THE thermal decomposition of ethylene iodide has been investigated in carbon tetrachloride solutions by Polissar.[1] Schumacher and Wiig[2] have studied the photochemical reaction also in carbon tetrachloride solutions. The reaction was found to be catalyzed by iodine atoms in both instances, the thermal reaction being governed by the rate expression,

$$-d[C_2H_4I_2]/dt = k[C_2H_4I_2][I_2]^{1/2},$$

while the equation

$$-d[C_2H_4I_2]/dt = k'I_{abs.}^{1/2}[C_2H_4I_2]$$

represents the photochemical rate.

In a slight modification of Polissar's interpretation Schumacher[3] has suggested the following mechanism for the decomposition of ethylene iodide: (1) $I_2 \rightarrow I+I$; (2) $C_2H_4I_2+I \rightarrow C_2H_4I+I_2$; (3) $C_2H_4I \rightarrow C_2H_4+I$.

This mechanism gives the rate expression,

$$-d[C_2H_4I_2]/dt = k_2K_{I_2}^{1/2}[C_2H_4I_2][I_2]^{1/2}$$

when it is assumed that the equilibrium concentration of C_2H_4I is very low, and that steps (1) and (3) are so fast that step (2) is the rate determining process.

In addition to the iodine catalyzed reaction Polissar found indications of an uncatalyzed decomposition of ethylene iodide, occurring simultaneously with the first reaction. This has been entirely disregarded by Schumacher in his discussion of the reaction mechanism.

The purpose of the present investigation was to compare the rate of the gas reaction with that in solution and also to establish definitely the presence of the uncatalyzed decomposition. On account of very considerable difficulties encountered, the results obtained are not as satisfactory as could be desired. Yet we believe them of sufficient value to be worthy of a brief description.

EXPERIMENTAL METHOD

The measurements were made by the static method. The increase in pressure was followed by a mercury manometer with an intervening quartz spiral gauge, which acted as a null-point instrument. The final form of the apparatus is shown diagrammatically in Fig. 1.

The ethylene iodide was prepared by passing ethylene gas into a saturated solution of iodine in absolute alcohol.[4] The product was washed on the filter with cold absolute alcohol and then recrystallized twice from absolute alcohol. Care was taken not to warm the alcoholic solutions above 50°C to prevent the formation of $CH_2ICH_2OC_2H_5$.[5] The ethylene iodide was kept in a pure form free from iodine on dry ice.

The first results obtained proved to be quite irreproducible. The final procedure, adopted after several unsuccessful modifications, was as follows: The system was thoroughly evacuated.

[1] Polissar, J. Am. Chem. Soc. **52**, 956 (1930).

[2] Schumacher and Wiig, Zeits. f. physik. Chemie **B11**, 45 (1930).

[3] Schumacher, J. Am. Chem. Soc. **52**, 3132 (1930).

[4] Semenoff, Jahresber. Fortschritte Chem **1864**, 483.

[5] Baumstark, Ber. **7**, 1172 (1875).

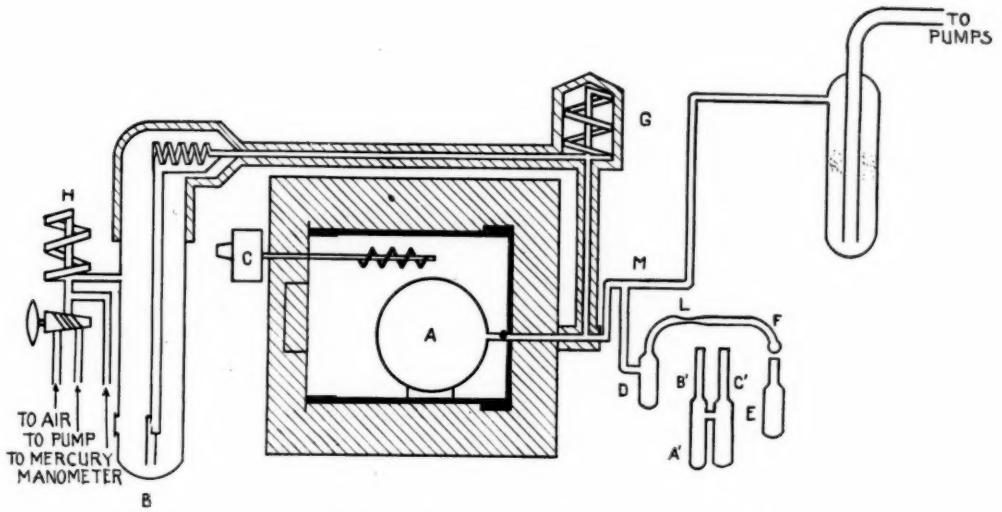


FIG. 1. The apparatus. *A*, reaction flask; *B*, quartz spiral manometer; *C*, De Khotinsky bimetallic thermoregulator; *D* and *E*, filling tubes; *G* and *H*, flexible spirals.

Air was let in through a slow leak and a large calcium chloride tube. Although the effect of moisture on the reaction was found to be negligible, its presence prevented satisfactory volatilization of the ethylene iodide at the start of a run, and thus a thorough drying of the system was essential. Tube *E*, containing ethylene iodide, was sealed on at *F*, care being taken to prevent flame products from entering the system. This precaution was found to be very essential to obtain reproducible results. After evacuation of the system the middle fraction of ethylene iodide was sublimed by gentle heating into *D*, and *E* was sealed off at *L*. Heating of ethylene iodide above the melting point was avoided, as rapid decomposition took place in the liquid phase.

The system was further evacuated while *D* was cooled with solid carbon dioxide, and was sealed off from the pump at *M*. The ethylene iodide was then volatilized into the reaction flask, and the exposed portions of the reaction system were covered with an auxiliary furnace already heated above the condensation point of the reaction mixture.

The products of the reaction were found to be completely condensable with liquid air, and the solid matter was entirely soluble in carbon tetrachloride. The final pressure remained constant within 0.3 mm over a period of several days, indicating that no polymerization of ethylene occurred. From this evidence and the doubling of the initial pressure, it was concluded that ethylene and iodine were the only reaction products.

In determining the effect of an excess of iodine on the rate it was found necessary to vaporize the ethylene iodide and the iodine separately. Otherwise iodine caused excessive decomposition of ethylene iodide. In these runs the vacuum distillation process was dispensed with the filling tube, *A'*, used. Ethylene iodide was placed in one side of it and iodine in the other. One side was sealed off and the other was attached to the system in place of the tube, *D*. The ethylene iodide was carefully vaporized first, and then the iodine.

RESULTS AND THEIR INTERPRETATION

At 195°C, on increasing the surface to volume ratio of the reaction flask four times, it was found that the reaction rate increased by a factor of about 1.8, indicating the presence of an appreciable surface reaction. At higher temperatures this heterogeneous reaction was not noticeable but even at 230°C the reaction went almost to completion in a very few minutes. These circumstances limited the accessible temperature range and made an accurate determination of the temperature coefficient impossible.

It was found that Polissar's expression for the iodine catalyzed reaction could not be fitted

to our results. They were best described by the equation,

$$-d[C_2H_4I_2]/dt = k_1[C_2H_4I_2] + k_2[C_2H_4I_2][I_2]^{1/2}.$$

This indicates the simultaneous occurrence of two reactions, namely, the iodine catalyzed reaction described by Polissar and Schumacher, and a unimolecular decomposition.

Fig. 2 and Fig. 3 give a plot of the quantity, $-d[C_2H_4I_2]/dt/[C_2H_4I_2]$ *vs.* $[I_2]^{1/2}$. Fig. 2 shows results at 478°K, 493°K and 503°K in an empty 500 cc Pyrex flask; Fig. 3 shows results at 478°K and 493°K in a similar flask filled with pieces of 10 mm Pyrex tubing which increased the total surface four times. The different runs are distinguished by characteristic markings.

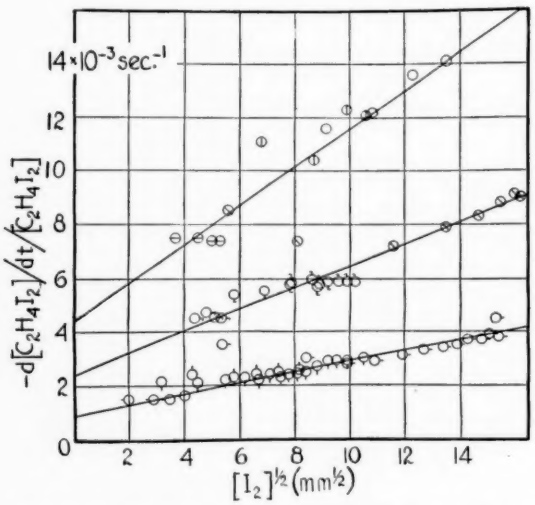


FIG. 2. A plot of $-d[C_2H_4I_2]/dt/[C_2H_4I_2]$ *vs.* $[I_2]^{1/2}$ for the empty reaction flask. Upper curve 503°K. Middle curve, 493°K. Lower curve, 478°K.

Some of the runs, particularly in the empty flask, show abnormally high initial velocities. This behavior was still much more pronounced in earlier runs not shown in the figures. As the technique of purifying the substance, evacuating and filling the reaction system was refined, the velocities became increasingly consistent with the rate expressions as given above. This is evidence that the deviations are due to extraneous causes, presumably some impurity eliminated by the more painstaking technique employed in the final series of experiments. In these plots the slopes of the straight lines drawn

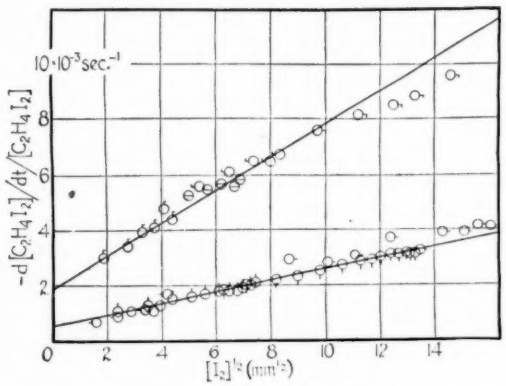


FIG. 3. A plot of $-d[C_2H_4I_2]/dt/[C_2H_4I_2]$ *vs.* $[I_2]^{1/2}$ for the filled reaction flask. Upper curve, 493°K. Lower curve, 478°K.

give the velocity constants of the iodine catalyzed reaction, while their intercepts with the ordinate axis are the velocity constants for the unimolecular reaction.

The values obtained in this manner are given in Table I.

The agreement of these results is not very good, but it shows without any doubt that the unimolecular reaction is existent and that both reactions are essentially homogeneous.

The activation energies obtained from the above data for the unimolecular reaction are 35,600 cal. for the unfilled flask and 37,600 cal. for the filled flask. They are 28,700 cal. and 32,800 cal., respectively, for the iodine catalyzed reaction. As our experimental results do not allow a satisfactory choice between these values, for the succeeding discussion we shall use the average values: 36,600 cal. for the unimolecular, and 30,200 cal. for the iodine catalyzed reaction. The uncertainty of these values is probably ±3000 cal.

The information obtained in these experiments on the unimolecular reaction is rather meager. From the agreement of the experimental data

TABLE I.

Temp.	Unimolecular reaction		Iodine catalyzed reaction	
	Empty flask	Filled flask	Empty flask	Filled flask
	(10^{-3} sec.$^{-1}$)		(10^{-4} mm$^{1/2}$ sec.$^{-1}$)	
478°K	0.9	0.5	1.78	2.0
493°	2.4	1.8	4.24	5.95
503°	4.4		7.12	

with the first order rate expression, it may be concluded that the falling off of the unimolecular velocity constant occurs at lower pressures than those studied, i.e., 25 mm to 250 mm initial pressure of ethylene iodide. Expressing the velocity constant in the form, $k = Ae^{-E/RT}$, it is found that the constant, A, is approximately 10^{13}. This is the same order of magnitude as is found in many other unimolecular reactions. The usual computation[6] shows that ethylene iodide has a sufficient number of degrees of freedom to maintain the necessary rate of activation.

The higher temperature coefficient of the unimolecular reaction explains why Polissar found only indications of an uncatalyzed reaction, while it is found to be quite prominent in the higher temperature range covered in this investigation.

As has been pointed out by Polissar and by Schumacher, the activation energy of the iodine catalyzed reaction is equal to one-half the heat of dissociation of the iodine molecule plus the heat of activation of the reaction between iodine atoms and the ethylene iodide molecules. The former is equal to 18,300 cal.[7] and the latter therefore is equal to 11,900 cal.$\pm$3000 cal. This value agrees within experimental error with those values found for the reaction in solution.[1, 2]

It is possible to calculate the number of collisions between iodine atoms and ethylene iodide molecules since the concentration of the iodine atoms is that of the thermal equilibrium and the latter is accurately known. At 478°K the dissociation constant of iodine is 3.75×10^{-9} mm Hg as calculated from the equation of Gibson and Heitler.[8] Assuming diameters of 4×10^{-8} and 3×10^{-8} cm for the ethylene iodide molecule and the iodine atom respectively, the total number of collisions at unit pressure between ethylene iodide and iodine molecules is 1.7×10^{18} cc^{-1} sec.$^{-1}$. The number of ethylene iodide molecules decomposing under the same conditions is 4.1×10^{13} cc^{-1} sec.$^{-1}$. The ratio of the two is 2.4×10^{-5}. This corresponds to an activation energy of 12,300 cal. if it is assumed that the entire activation energy is contained in only two degrees of freedom and that the steric factor is unity.

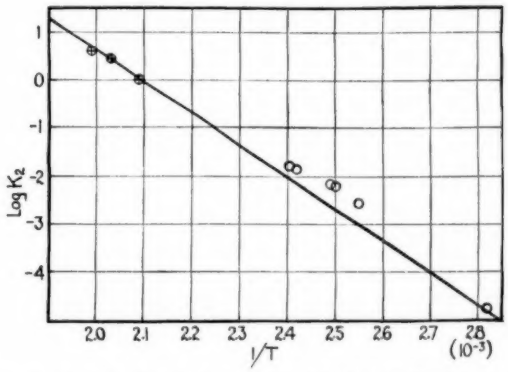


FIG. 4. A plot of log k *vs.* $1/T$. Circles, Polissar; circles with crosses, Arnold and Kistiakowsky.

It is of some interest to compare the absolute reaction rates in solution and in the gas phase. Fig. 4 shows a plot of the logarithms of the constants (mols$^{-1/2}$ cc$^{1/2}$ sec.$^{-1}$) for the iodine catalyzed reaction determined by Polissar and those (average) from this investigation plotted against the inverse temperature. The straight line drawn through our points corresponds to an activation energy of 31,400 cal. It will be seen that Polissar's values differ from our extrapolation only by about a factor of two. Considering the uncertainties of the extrapolation, one may conclude that the reaction velocity in solution and in the gas phase are essentially the same and that the solvent has very little influence, not only on the activation energy, but also on the collision frequency between the reacting molecules.

In conclusion it may be pointed out that the gaseous decomposition of ethylene iodide is one of the very few reactions in which two entirely independent reaction mechanisms occur with essentially equal rates in the same temperature range to give the same final products. In this respect ethylene iodide occupies a position intermediate between hydrogen iodide and hydrogen bromide. The second of these, as is well known, decomposes exclusively through atomic chains, while the other decomposes bimolecularly. The latter, and not a unimolecular reaction, is to be expected, of course, because the hydrogen iodide molecule contains only one atom of iodine and, furthermore, has only a few degrees of freedom.

[6] Kassel, *Kinetics of Homogeneous Gas Reactions*, New York, Chemical Catalog Company, 1932.

[7] Bodenstein and Stark, Zeits. f. Elektrochemie **16**, 961 (1910).

[8] Gibson and Heitler, Zeits. f. Physik **49**, 465 (1928).

Vapor Viscosities and the Sutherland Equation

J. HOWARD ARNOLD, *School of Chemistry, University of Minnesota*

(Received December 2, 1932)

Reversing the usual procedure of calculating molecular diameters from the kinetic-theory viscosity equation, it is suggested that the Sutherland constant be found, to serve as a criterion for the accuracy of this constant as obtained from viscosity-temperature data. The molecular diameter is taken proportional to the cube root of the molar volume of the liquid at the boiling point, as indicated by the theory of corresponding states; the error is small. Review of the available values of C indicates that many of them are erroneous, because of experimental error, magnified by extrapolation, or possible failure of the Sutherland equation. The Vogel rule, $C=1.47T_b$, is found valid to within 10 percent. The recent data of Braune and Linke, Melaven and Mack, and Lowry and Nasini are criticized.

TO represent the temperature variation of the viscosity of a gas, Sutherland[1] has derived the equation

$$Z=[A(M)^{1/2}/s^2][T^{1/2}/(1+C/T)]. \quad (1)$$

For the evaluation of the Sutherland constant C from viscosity-temperature data, Eq. (1) is generally utilized in the form

$$T^{3/2}/Z=[s^2/A(M)^{1/2}](T+C). \quad (2)$$

On plotting $T^{3/2}/Z$ against T, a straight line results, having an intercept $-C$ on the T axis. It is well known that C determined in this manner is very sensitive to errors in Z (or T), a 1 percent error in Z being reflected to C as a deviation of 8 percent to 12 per cent. When only two points on the line are known, incidental experimental errors may lead to a very inaccurate value of C. Even when a number of points is available, the value of C may be erroneous because of errors in Z varying systematically with T, and hence remaining undetected. Moreover, high precision in vapor viscosity measurements is difficultly attainable; the literature consequently contains many grossly incorrect values of C.

To serve as a criterion of the accuracy of experimental measurements of vapor viscosities, an alternative method of finding the Sutherland constant is desirable. Unfortunately, no practical method of evaluating this constant from theoretical considerations has yet been proposed. Rankine[2] noted that C is roughly proportional to the critical temperature, and advanced the equation

$$C=T_c/1.12. \quad (3)$$

Vogel[3] later proposed the similar relationship

$$C=1.47T_b. \quad (4)$$

However, both these rules are empirical and only approximate, though useful for rough estimates.

Trautz,[4] in recent papers, has suggested as an accurate general relationship at the critical temperature

$$d\ln Z/d\ln T=m=1. \quad (5)$$

However, differentiation of Eq. (1) leads to

$$d\ln Z/d\ln T=3/2-T/(T+C) \quad (6)$$

from which it is evident on inspection that Eq. (5) can hold only if $C=T_c$. Comparison with Eq. (3) indicates that the Trautz expression is only an approximately valid special case of the Sutherland equation. Deviations from Eq. (5) are less noticeable than those from Eq. (1), a 4 percent error in C being equivalent to a 1 percent error in m.

It is apparent from an inspection of Eq. (1) that (since A is a universal constant) if the value of s were known, C could be calculated directly from a single point on the viscosity-

[1] Sutherland, Phil. Mag. **36**, 507 (1893).

[2] Rankine, Phil. Mag. **21**, 45 (1911).

[3] Vogel, Ann. d. Physik **43**, 1235 (1914).

[4] Trautz, Ann. d. Physik **10**, 263; **11**, 190 (1931).

temperature curve, with an accuracy of the same order as that to which Z and s are known. Titani[5] and the writer[6] have pointed out that s may, with considerable accuracy, be taken proportional to the cube root of the molar liquid volume at the normal boiling point:

$$s = 10^{-8} V^{1/3}. \quad (7)$$

The *approximate* truth of this proportionality was shown many years ago by Lothar Meyer[7] and his coworkers. Its theoretical basis is the van der Waals theory of corresponding states, by which the molecules of all substances occupy the same fraction of the total volume of the liquid, at identical reduced temperatures and pressures. The extensive tests of this theory by Sydney Young[8] and others have shown that, while for the gaseous state it is only roughly true, its accuracy is much greater for liquids. For most substances, the boiling point is nearly the same fraction of the critical temperature, on the absolute scale. Since the rates of change of liquid volume with pressure and temperature are small, no great error is made in taking the boiling points of all substances to be one and the same reduced temperature, and setting the boiling-point volume proportional to the actual volume of the molecules. There remains, of course, the question whether the kinetic theory s is the same as the actual diameter; no reason for doubting this equality is apparent.

Eliminating s between Eqs. (1) and (7), and solving for C,

$$C^* = 2.70 \times 10^{-5} (M^{1/2} T^{3/2} / Z V^{2/3}) - T. \quad (8)$$

The value of A used here is that resulting[6] from the classical kinetic theory as given by Jeans.[9] From this equation C may be found with an accuracy considerably greater than that afforded by Eq. (2), a 1 percent error in Z giving rise to an error of about 2 percent in C, as contrasted to 8 percent to 12 percent from Eq. (2).

Table I contains the values of C calculated by the four methods listed—Eqs. (8), (2), (4), and (3)—for the substances listed by Titani.[5]

[5] Titani, Bull. Chem. Soc. (Japan) **5**, 98 (1930).
[6] Arnold, Ind. Eng. Chem. **22**, 1091 (1930).
[7] Meyer, Ann. d. Physik **16**, 394 (1882).
[8] Young, Phil. Mag. **33**, 168 (1892).
[9] Jeans, *The Dynamical Theory of Gases*, p. 276.

TABLE I. *Data of Titani.*

	Z_0	V	M	C^*	C	$1.47T_b$	$\frac{T_c}{1.12}$
Ethane	863	56.7	30	248	287	265	274
Propane	751	74.6	44	333	341	336	330
n-Butane	682	96.0	58	372	377	402	378
Isobutane	689	(95.7)	58	367	336	386	364
Ethylene	907	(49.3)	28	254	259	248	252
Propylene	783	(67.2)	42	335	322	332	330
Butylene 1 : 2	708	(86.9)	56	382	329	364	
Butylene 2 : 3	694	86.9	56	396	362	403	
Isobutylene	732	(86.6)	56	362	339	392	378
Isoamylene	665	110.1	70	392	368	430	
Acetylene	954	41.9	26	267	198	278	275
Allylene	808	59.8	40	349	277	354	360
Cyclopropane	807	60.2	42	360	372	350	326
Methyl ether	850	62.6	46.1	342	345	366	357
Methyl chloride	983	50.4	50.5	371	380	366	372
Methyl bromide	1228	55.7	93	380	379	408	408

T_b and T_c have been taken from the *International Critical Tables* and the *Landolt-Börnstein Tabellen*, while the values of V are to be found in the compilation of LeBas.[10] In a few cases where the observed values of V are not given, these have been calculated by LeBas' methods, and are shown in parentheses. Considering the approximate nature of Eqs. (3) and (4), the agreement throughout is excellent; it is noteworthy that for acetylene and allylene C^* corresponds closely to $1.47T_b$, though considerably higher than the experimental C. The average deviation of C^* from C is 8.6 percent; of C^* from $1.47T_b$, only 4.3 percent. Titani's value for the viscosity of ethylene has been checked closely by Zimmer,[11] and that for propane by Klemenc and Remi[12]; the latter also give C as 324, compared to Titani's 341. Breitenbach[13] has investigated ethylene and methyl chloride, giving Z at 15° as 1011 and 1057, respectively, from which C^* is 227 and 403.

Table II contains the data of Rankine[14, 15] and his coworkers, Smith[16] and Harle.[17] The values of C were obtained from viscosity measurements at only two temperatures, and consequently cannot be expected to be very accurate. The average deviation of C from C^* is 15 percent; of C^* from $1.47T_b$, only 7 percent.

[10] LeBas, *The Molecular Volumes of Liquid Chemical Compounds*, Longmans, Green and Company, London, 1915.
[11] Zimmer, Verh. Deut. Phys. Ges. **14**, 471 (1912).
[12] Klemenc and Remi, Monats. f. Chem. **43**, 307 (1923).
[13] Breitenbach, Ann. d. Physik **67**, 803 (1899).
[14] Rankine, Proc. Roy. Soc. **A86**, 162 (1911).
[15] Rankine and Smith, Phil. Mag. **42**, 601, 615 (1921).
[16] Smith, Proc. Roy. Soc. **A106**, 83 (1924).
[17] Harle, Proc. Roy. Soc. **A100**, 429 (1921).

TABLE II. *Data of Rankine, Harle and Smith.*

	t	Zt	V	C^*	C	$1.47T_b$	$\frac{T_c}{1.12}$
Chlorine	12.7	1290	45.4	383	325	352	372
Bromine	12.8	1510	53.6	484	460	487	513
Iodine	124	1840	68.0	713	590	672	737
Hydrogen chloride	12.5	1385	33.1	264	357	276	290
Hydrogen bromide	18.7	1819	(35.5)	328	375	302	324
Hydrogen iodide	20.6	1873	(45.5)	348	390	348	378
Hydrogen sulfide	17	1251	(33.0)	311	331	312	333
Water	100	1270	18.7	548	650	548	570
Ammonia	100	1303	25.2	342	370	352	362
Phosphine	15	1129	(38.1)	314	290	273	289
Arsine	15	1552	(38.9)	368	300	320	
Methane	17	1094	38.0	140	198	160	170
Silicane	15	1124	(46.8)	218	229	236	
Cyanogen	17	995	60.4	336	330	370	356
Carbonyl sulfide	15	1190	(48)	364	330	330	338

Note that if the entire 15 percent deviation be attributed to an error in Z, this need amount to only 1.5 percent, not at all unusual in vapor viscosity measurements. For ammonia, Edwards and Worswick[18] found $C=377$, while from their data ($Z=1005$ at 15°) C^* is found to be 343, practically identical with the 342 of Rankine and Smith. For hydrogen chloride, a C^* of 258 results from the measurements ($Z=1434$ at 21°) of Trautz and Narath,[19] who also found $C=362$. The graphical evaluation of C from the data of Trautz and Winterkorn[20] gives 294 for chlorine and 298 for hydrogen iodide, the line (Eq. (2)) for the latter substance being noticeably curved. For chlorine, Z at 20° is 1312, whence $C^*=387$, and for hydrogen iodide Z is 1857 at 20.5°, $C^*=354$. Though the agreement with Rankine is excellent for C^*, the two values of C last given are much lower; with these corrosive substances, high precision is not to be expected, however.

All the above-mentioned data have been obtained with the capillary-flow method. Table III contains the results of Vogel[3] and of Suhrmann[21] by the oscillating-disk method; of Day,[22] by the rotating-cylinder method; and of Ishida,[23] who used the Millikan oil-drop method. All four investigators worked at a single temperature, so no values of C were determined. In the last column of the table, for comparison, values of C^* resulting from capillary-flow measurements are given. An indication of the agreement of the various methods with that of capillary flow may be had by comparing values of C^* for the same substance; this amounts to a comparison of viscosities, but eliminates the necessity for reduction to a common temperature. Thus, the values of C^* from Vogel's data show a mean deviation from the corresponding values from capillary-method data of 3.3 percent, indicating a discrepancy in the actual viscosities of about half this amount, 1.7 percent. (It is not certain whether Vogel's data for methyl bromide refer to this substance or to ethyl bromide, both designations appearing at various points in his paper.)

TABLE III.

	Z	V	C^*	$1.47T_b$	$\frac{T_c}{1.12}$	$C^*_{cap.}$
Data of Vogel (0°)						
Methane	1025	38.0	147	160	170	140
Ethane	848	56.7	259	265	274	248
Acetylene	936	41.9	276	278	275	267
Methyl chloride	971	50.4	377	366	372	371
Methyl bromide	1028	55.7	508	408	408	380
Ethyl chloride	936	71.7	331	420	407	
Chloroform	937	84.5	463	490	475	470
Ethyl acetate	685	106.1	465	515	467	477
Ethyl ether	679	106.2	412	452	417	432
Ammonia	919	25.2	362	352	362	342
Water (at 29°)	998	18.7	553	548	570	548
Data of Suhrmann (14.2°)						
Ethyl ether	716	106.2	415	452	417	432
Carbon disulfide	964	62.1	472	470	488	
Chloroform	989	84.5	470	490	475	470
Benzene	738	96.0	463	520	501	507
Data of Day (25°)						
n-Pentane	673	117.8	430	455	420	
Isopentane	691.5	117.4	410	442	411	403
Data of Ishida (23°)						
Methane	1079	38.0	179	160	170	140
Ethane	927	56.7	277	265	274	248
Isobutane	755	(95.7)	382	386	364	367

The experimental error in vapor viscosity determinations appears to be of the order of magnitude of 1 percent; errors of 1–2 percent are generally sufficient to explain the differences between C and C^*. The agreement between C^* and the $1.47T_b$ given by the Vogel rule is surprisingly close, 10 percent or better in practically all cases. From these two salient facts, it seems reasonable to conclude that discrepancies between C and C^* are largely traceable to experimental inaccuracy in C.

In the light of this conclusion, additional vapor viscosity data may now be considered. Table IV contains data reported by Braune,

[18] Edwards and Worswick, Proc. Phys. Soc. **A38**, 16 (1925).

[19] Trautz and Narath, Ann. d. Physik **79**, 637 (1926).

[20] Trautz and Winterkorn, Ann. d. Physik **10**, 511 (1931).

[21] Suhrmann, Zeits. f. Physik **14**, 56 (1923).

[22] Day, Phys. Rev. **40**, 280 (1932).

[23] Ishida, Phys. Rev. **21**, 550 (1923).

Basch, and Wentzel[24] and Braune and Linke,[25] who used the oscillating-disk method. Their viscosities have been calculated by reference to air at room temperature as a standard. Their high-temperature data for air do not conform to the Sutherland equation with the generally-accepted value of $C=118$, but require a C of 135. The work of Edwards,[26] in refutation of the conclusions of Williams,[27] indicates that no high-temperature abnormalities are present; Williams found a sharp break in the curve, undoubtedly due to experimental error. Braune, Basch and Wentzel, "correcting" Williams' data on the assumption that his low-temperature values were erroneous, were able to bring his data into agreement with their own. Nevertheless, the

TABLE IV. *Data of Braune and Linke.*

	V	t	Z_t	C^*	C	$1.47T_b$	$C_{cap.}$	$C^*_{cap.}$
Water	18.7	20.1	937	574	961	548	650	548
		93	1178	604				
Ammonia	25.2	17	982	371	626	352	370	342
Hydrogen cyanide	38.8	21	740	440	901	441		
Chlorine	45.4	16	1294	386	351	352	325	383
Bromine	53.6	516	3967	546	533	487	460	484
Iodine	68.0	232	2319	765	568	672	590	713
Methyl chloride	50.4	20	1033	390	441	366	380	371
Methylene chloride	65.1	22	991	490	425	460		
Chloroform	84.5	20	1001	474	461	490		470
Carbon tetrachloride	103.7	258	1676	573	492	515	470	532

higher value of C required points to experimental inaccuracy, which apparently extends also to the vapor viscosity measurements of Braune and Linke. The values of C are in some cases much too large; this is especially noticeable for ammonia and water. The average deviation of C^* from $1.47T_b$ is 7.9 percent; excluding the four high-temperature values, it is 5.3 percent, compared to 4.3 percent for Titani's data. In Table IV, the viscosities used for calculation of C^* have been taken in most instances at the lowest available temperature.

The viscosity of water vapor has been determined by a number of investigators. Speyerer[28] gave C as 673, and Z at 100° as 1279.2, from

[24] Braune, Basch and Wentzel, Zeits. f. physik. Chemie **137**, 176 (1928).

[25] Braune and Linke, Zeits. f. physik. Chemie **148**, 195 (1930).

[26] Edwards, Proc. Roy. Soc. **A117**, 245 (1927).

[27] Williams, Proc. Roy. Soc. **A110**, 141 (1926); **A113**, 233 (1927).

[28] Speyerer, Forschungsarb. Ver. Deutscher Ing., No. 273 (1925).

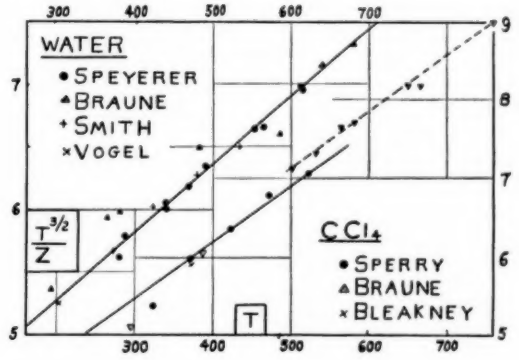


FIG. 1. Comparisons of viscosity data, illustrating magnitude of experimental errors.

which $C^*=546$. From Vogel's determination at 29° (Table III) C^* is 553. Smith's data do not show good agreement with the Sutherland equation, giving a curved line; he estimated C as 650, while C^* from his work is 548. Braune and Linke's C of 961 is certainly erroneous; from their two lowest-temperature points, C^* is found to be 574 and 604. Fig. 1 shows the data of all these investigators plotted according to Eq. (2). Smith, Speyerer and Vogel agree very well; Braune and Linke's points, however, depart from the straight line by as much as five percent, approaching it at the highest temperatures. The values of C^* lie remarkably close to that of $1.47T_b$, 548; C appears to be about 600 or 650, though the data are hardly accurate enough to permit its exact determination.

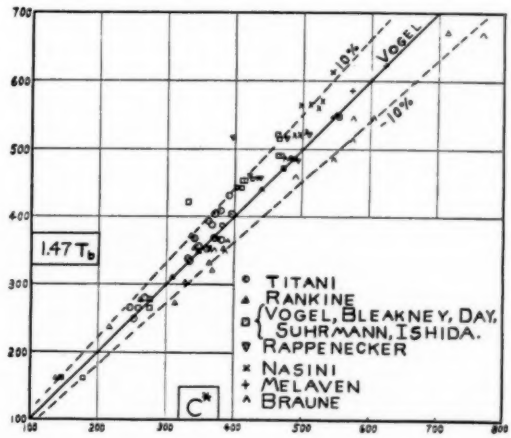


FIG. 2. The relation of the Sutherland constant to the absolute boiling-point; showing the approximate (±10 percent) validity of the Vogel equation.

Fig. 1 also shows the data of three investigators for carbon tetrachloride. The points representing the data of Sperry and Mack[29] (by the capillary method) lie along a line parallel to the line through the points of Braune and Linke, but about 3 percent below it. The single point of Bleakney[30] is close to the Sperry-Mack line. Apparently by giving undue weight to the point at 50°, which is out of line with the others by nearly 5 percent, Sperry and Mack found a C of 335, though $C=470$ gives better agreement with the other points. Even this revised value of C, however, differs considerably from that of C^*, 532.

Table V contains the recent results of Lowry and Nasini,[31, 32] by the capillary-flow method. The average deviation of C^* from $1.47T_b$ is 7.7 percent. The values of C are uniformly lower than those of C^*, and show the peculiar property of decreasing with increasing molecular weight in homologous series. Thus, the values of C for toluene and methyl thiophene are lower than those for benzene and thiophene. A similar behavior, much more pronounced, has been found by Melaven and Mack[33] in the paraffin series (Table VI): heptane, 445; octane, 337; nonane, 276. This rapid decrease in C produces a correspondingly rapid increase in the molecular collision areas. They have advanced reasons for believing that the Vogel rule might fail for very large molecules; however, there is no apparent reason for supposing that the agreement between C and C^* found in the preceding paragraphs should be dependent upon molecular size. Table VI, in fact, shows an excellent agreement between C^* and $1.47T_b$, as is to be expected. It is highly probable, therefore, that this behavior of C arises from experimental inaccuracies, which are greatly magnified in the calculation of the Sutherland constant. Such errors need not be excessively large; for example, a maximum deviation of 8 percent at one end of the curve for nonane is sufficient to cause the observed difference between C^* (622) and C (276). It is noteworthy that neither Lowry and Nasini nor Melaven and Mack mentioned any calibration of their apparatus with air; the latter, however, checked Lowry and Nasini's data for toluene closely. Viscosities, in both cases, were calculated from the theoretical formula. (For the viscosity of heptane, Melaven and Mack's value of 1080 at 251.6° is evidently a misprint for 1008.)

TABLE V. *Data of Lowry and Nasini.*

	t	Z	V	C^*	C	$1.47T_b$	$\frac{T_c}{1.12}$
Benzene	100	940	96.0	497	380	520	501
Toluene	96	880	118.3	496	370	563	530
Cyclohexane	104	880	116.3	489	330	520	494
Thiophene	96.2	1031	85.1	506	407	525	527
Methyl thiophene	100	965	(107.3)	511	400	565	
Pyridine	98.2	958	89.5	529	320	570	551
Acetic acid	249.5	1504	63.7	523	725	560	530

Additional evidence that the values of C are erroneous may be obtained from a comparison of the collision areas. In Table VII are shown the molecular cross-sectional areas calculated with the use of the Sutherland constants C and C^*, the areas being respectively $\bar{A}$ and $(\pi/4)V^{2/3}$. Melaven and Mack have also determined molecular areas by shadowgraphic measurement of models constructed to scale from x-ray data. Four shadow-areas are given, for various spatial arrangements of the hydrocarbon chain: tight helix, loose helix, extended chain and sphere of revolution. With increase in chain length, $\bar{A}$ increases at a very rapid rate (because of the decrease in C)—faster than any shadow area except that of the sphere of revolution, for which the absolute values of the area are several times too large. On the other hand, the areas found from C^* correspond satisfactorily with

TABLE VI. *Data of Melaven and Mack (100°).*

	V	Z	C^*	C	$1.47T_b$	$\frac{T_c}{1.12}$
Heptane	162.8	717	544	445	546	482
Octane	(185.0)	675	573	337	586	508
Nonane	(207.2)	633	621	276	622	525

TABLE VII. *Comparison of collision areas.*

	$\bar{A}$	$(\pi/4)V^{2/3}$	Tight	Loose	Extended	Sphere
Heptane	26.7	23.5	23.7	30.0	34.8	93.3
Octane	34.9	25.5	25.0	34.5	38.7	116.8
Nonane	42.5	27.5	25.6	38.0	43.0	143.1

[29] Sperry and Mack, J. Am. Chem. Soc. **54**, 904 (1932).
[30] Bleakney, Physics **3**, 123 (1932).
[31] Lowry and Nasini, Proc. Roy. Soc. **A123**, 686, 692 (1929).
[32] Nasini, Phil. Mag. **8**, 596, 601 (1928).
[33] Melaven and Mack, J. Am. Chem. Soc. **54**, 888 (1932).

the shadow areas given by the tight-helix arrangement, both in absolute value and in rate of increase.

That the capillary-flow method of vapor viscosity measurement is subject to serious error has long been recognized,[34] especially since the work of Schumann[35] and Steudel,[36] who ascribed their difficulties to condensation in the capillary. The effect of such errors is well shown by the results of Rappenecker,[37] Table VIII. Ethyl

TABLE VIII. *Data of Rappenecker (100°).*

	Z	V	C^*	C	$1.47T_b$	$\frac{T_c}{1.12}$
Benzene	930	96.0	507	700	520	501
Isopentane	885	117.4	403	500	442	410
Ethyl ether	967	106.2	432	325	452	417
Methyl acetate	1015	83.8	487	660	485	453
Ethyl acetate	955	106.1	477	650	515	467
Chloroform	1307	84.5	470	292	490	476
Acetone	943	77.1	492	670	484	453
Ethyl alcohol	1090	62.1	397	525	516	461

alcohol appears to be anomalous, having C^* much lower than $1.47T_b$; the discrepancy is apparently not due to experimental error, as Rappenecker's viscosity has been checked closely by Pedersen[38] by the same method. Excluding alcohol, the mean deviation of C^* from $1.47T_b$ is 4.4 percent, comparing favorably with 4.3 percent for Titani's results. The values of C are very erratic, some too high and others too low; they are based on data at only two temperatures, and greatly influenced by small errors in Z.

In Table IX are shown the data of Bleakney,[30] by the rotating-cylinder method. Though C^* and $1.47T_b$ agree well, all values of C are much lower, and have been found from data at only two temperatures, 25° and 100°.

The frequent lack of agreement between C and C^* may be attributed to three causes: (1) the incorrectness of Eq. (7), upon which the calculation of C^* is based; (2) the failure of the Sutherland equation itself; and (3) experimental error. The first is hardly capable of giving rise to deviations of the magnitude found; thus, to obtain a C^* agreeing with Bleakney's C of 299

TABLE IX. *Data of Bleakney (25°).*

	Z	V	C^*	C	$1.47T_b$
n-Pentane	676	117.8	427	299	455
Isopentane	695	117.4	407	268	442
2-Pentene	689	(110.5)	435	304	455
Trimethyl ethylene	701	110.1	422	283	458

for pentane, a V of 158 (instead of 117.8) must be used in Eq. (8). It is highly improbable that any such inaccuracy is attached to Eq. (7).

The permanent gases, at low temperatures, exhibit deviations from the Sutherland equation in such a direction as to lower the value of C found from Eq. (2). Chapman[39] has pointed out that for vapors similar deviations should occur at relatively higher temperatures. However, the experimental evidence on this point is inconclusive. Rankine[40] and Braune, Basch and Wentzel[24] observed the appearance of such deviations for bromine vapor at about room temperature; for ethylene, Zimmer[11] made a similar observation. Nevertheless, throughout the extensive experiments of Titani,[5] Braune and Linke,[25] Lowry and Nasini,[31] and Melaven and Mack,[33] regular departure of all vapors from the Sutherland law was *not* observed in the temperature range covered, from 20° up. If, as Bleakney suggests, the low values of C are due to the failure of the Sutherland equation, the behavior should be general. For Braune and Linke's data, C is generally too high; Titani's values are about right; others are much too low. Though deviations from the Sutherland equation may account for a part of the discrepancy between C and C^*, experimental inaccuracy certainly contributes. It is peculiar that the data available do not give a more definite indication of the cause of the difficulty.

CONCLUSIONS

(1) By the use of molecular diameters calculated from boiling-point volumes, together with viscosity determinations at a single temperature, Sutherland constants (C^*) may be determined. These in general agree well with the usual C found from the variation of viscosity with temperature.

(2) Vapor viscosity determinations are subject

[34] Brillouin, *Lecons sur la Visc. des Liq. et des Gaz*, Gauthier-Villars, Paris, 1907, II, p. 32.

[35] Schumann, Ann. d. Physik **23**, 253 (1884).

[36] Steudel, Ann. d. Physik **16**, 369 (1882).

[37] Rappenecker, Zeits. f. physik. Chemie **72**, 695 (1910).

[38] Pedersen, Phys. Rev. **25**, 225 (1907).

[39] Chapman, Phil. Trans. **211**, 433 (1911); **216**, 279 (1916).

[40] Rankine, Proc. Roy. Soc. **A88**, 575 (1913).

to errors of the order of 1 percent, which appears in C as an error of about 10 percent. Errors of similar magnitude may arise from the failure of the Sutherland equation at low temperatures. In either case, the use of this apparent C for the calculation of molecular diameters leads to large errors in the diameters.

(3) The Vogel equation, $C=1.47T_b$, reproduces the values of C^* with a mean error of 5 percent, and a maximum error of 10 percent. It may therefore be used as a fairly accurate empiricism.

(4) A survey of recent work on vapor viscosity reveals that many of the Sutherland constants reported deviate widely from the values of C^*, because of systematic experimental error or undetected failure of the Sutherland equation.